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The Pt/Au Thermocouple

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Part I: Essential Performance

Part II: Preparatory Heat Treatment,
Wire Comparisons and Provisional Scale

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THE Pt/Au THERMOCOUPLE: I. ESSENTIAL PERFORMANCE

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ABSTRACT

Studies of the properties of the Pt/Au thermocouple have been undertaken to find a superior and practical sensor as an alternative to the standard Pt/Pt10Rh thermocouple for temperature measurements in the range (0-1000)°C. Accounts of these studies are presented in two parts; I, Essential Performance and II, Preparatory Heat Treatment, Wire Comparisons and Provisional Scale. Part I examines the essential thermoelectric performance, following a recommended preparatory heat treatment, of the Pt/Au thermocouple at the ice point and at the freezing and melting temperatures of high purity metals including the In, Sn, Zn, Sb and Ag points. Significant stress-TEMFs arising from differential thermal expansions of the Pt and Au elements in regular junction sheathed (RJS) Pt/Au thermocouples were observed and amounted to the equivalent of $< 0.04^{\circ}\text{C}$ at the Sb and Ag points. This stress-TEMF can be eliminated simply by welding a weak stress-relieving Pt coil between the Pt and Au elements to form a stress-relieved junction sheathed (SRJS) Pt/Au couple. Insertion-withdrawal immersion-TEMF profiles in the fixed points were measured to assess

thermoelectric inhomogeneities along the thermoelements in the fixed points for both SRJS couples and individual elements; at greater than the threshold immersions for thermal conduction loss, thermoelectric inhomogeneities equivalent to $< 0.01^{\circ}\text{C}$ per 10 cm were typical. Time-TEMF curves at fixed immersion during freezing and melting were obtained to determine both the thermoelectric stability of the SRJS Pt/Au couple and the plateau temperature stabilities of the fixed point realizations — stabilities well inside the equivalent of 0.01°C/h are readily attained. Alloy melting range parameters derived from melting curves following slow freezing may be used reliably to select the thermometrically purest samples for high quality metal fixed points. The freezing temperatures of Ag and Sb increase 8 and 1 mK/atm, respectively, in good agreement with measurements by resistance thermometer and by thermo-chemical calculations. Direct comparisons at high precision of the immersion-TEMF characteristics of the Pt/Au and the Pt/Pt10Rh thermocouples at the metal fixed points are presented and critical assessments of the merits of these thermocouples for temperature measurements in the range $(0-1000)^{\circ}\text{C}$ are drawn. The stress-relieved Pt/Au couple clearly outclasses the Pt/Pt10Rh couple in thermoelectric stability, homogeneity and sensitivity ($19.6, 24.8 \mu\text{V}/^{\circ}\text{C}$, respectively, at Sb and Ag points compared to $10.3, 11.4 \mu\text{V}/^{\circ}\text{C}$, respectively for Pt/Pt10Rh) and even challenges the high temperature platinum resistance thermometer on the basis of simplicity and economic practicality. The Pt/Au couple, therefore, merits serious consideration as an alternative but preferred temperature sensor for many, if not most, precise (order $\pm 0.01^{\circ}\text{C}$) temperature measurements in the range $(0-1000)^{\circ}\text{C}$.

INTRODUCTION AND PURPOSE

Studies of the properties of the platinum/gold (Pt/Au) thermocouple in the range (0-1000)°C have been undertaken to find a superior but still a relatively simple and inexpensive sensor as an alternative to the standard Pt/Pt10Rh thermocouple, currently both the designated interpolation instrument [1] and the most commonly used thermoelectric sensor for precise temperature measurements in the range (630-1064)°C IPTS (1968). The Pt/Pt10Rh thermocouple suffers serious alterations in thermoelectric homogeneity along its immersed length (principally on the alloy element) when used at temperatures greater than 200°C [2-7]; the inhomogeneity limits the accuracy attainable in thermometry, the basic tenet of which assumes thermoelectric homogeneity in both thermoelements of the couple. There is a need in both science and industry for a simple and rugged sensor, capable of reliable temperature sensing to ± 10 or 20 mK, and accurate and stable for reasonable periods to a few centidegrees, to ensure dependable measurements of temperature to accuracies of better than 0.1°C.

Over the past 20 years the high temperature platinum resistance thermometer (HTPRT) has been developed [8-15] to meet and even surpass these requirements; at the present time there is an expectation [16] that the HTPRT will replace the standard thermocouple as the preferred interpolation instrument on the IPTS. High temperature platinum resistance thermometry will be neither simple nor inexpensive and in the foreseeable future probably will be used mostly in national standards laboratories. Thermoelectric thermometry, as

now, will continue to be used more generally for the majority of precise temperature measurements in the range (500-1000)°C. We believe that the Pt/Au thermocouple is an impressive contender for this task.

The literature on the Pt/Au thermocouple is extremely sparse. Roeser and Wensel [17] give a table of thermoelectric force (TEMF) vs temperature that was determined at NBS (Washington) prior to 1939. Recent determinations by Roberts [18] "agreed" with this NBS table over the range (273-900) K. We have found no reference that advocates the Pt/Au couple as a superior alternative to the standard Pt/Pt10Rh thermocouple for measurements to 1000°C. Preliminary investigations in this laboratory [2] using thermometric grade Pt and inferior 49 grade (99.99 wt % purity) Au elements showed enough promise of real improvement in thermoelectric homogeneity in Pt/Au couples to justify the present study on the preparation, properties and use of this couple in the range (0-1000)°C.

Part I examines the essential thermoelectric properties of the Pt/Au couple at the fixed points; Part II, of basic importance, will discuss the effects of preparatory heat-treatments on the subsequent thermoelectric stability and homogeneity of many Au and Pt thermoelements differing in purity, refiner, and refining batch.

APPARATUS AND METHODS

Complete descriptions of the form and preparation of Pt/Pt10Rh thermocouples and the measurement techniques used at the metal fixed points to determine the stability and thermoelectric

inhomogeneity along thermoelements assembled as a unit couple, and along individual elements assembled as the movable elements in type MJ-1 [19] special research couples are given in references [2-5].

The Pt/Au couples used in this study were also fabricated with 186 cm long thermoelements which were pulled into 2-bore recrystallized alumina sheaths (61 cm long, 1.3 mm bore) and lead-insulating harnesses designed to provide firm support and prevent unnecessary deformation of the thermoelements during assembly and during the insertion-withdrawal incursions (probe rate 1 cm/2 min) into the fixed points that are required for assessments of thermoelectric inhomogeneity.

Platinum elements were given regular NRC anneals [2, 3]: preparatory anneal — 10 h electric bare wire anneals (WA) at 1300°C in air, then quenched (abrupt current switch-off) to room temperature and followed by a 1 h bare WA at 450°C; maintenance anneal — 10 min 1300°C WA, quench, 1 h bare WA at 450°C; after assembly, the full length of the sheathed hot junction segment of the couple receives a further overnight finishing vacancy anneal at 450°C. The high temperature anneal stabilizes the thermopower against rapid changes in the high order defect and chemical impurity concentrations under sustained heat treatment at 1100°C; the low temperature finishing anneal at 450°C removes excess vacancies retained from the air-quench at 1300°C.

Gold elements, unless otherwise indicated, were prepared with 10 h furnace anneals (FA) at 1000°C: three 62 cm segments (later rewelded into a 186 cm thermoelement) were simultaneously annealed in

separate silica wells in an Inconel block furnace balanced over the segment length to ± 1 K at 1000°C. The sheathed segment of the assembled Pt/Au couple receives the regular NRC low temperature finishing vacancy anneal — overnight at 450°C. This preparatory anneal for gold wire was selected as a "preferred anneal" on the basis of a substantial investigation of the effects of heat treatment on the stability and thermoelectric homogeneity of high purity gold wires, details of which will be included in Part II of this study.

The Seebeck TEMFs were measured both manually using six-figure potentiometers (Guildline Instr. Ltd., Type 9180-B) with nanovolt null detectors (Keithley Instr. Inc., Type 147), and automatically using a computer acquisition system fed from a digital nanovoltmeter (Keithley Type 181).

BASIC PERFORMANCE AND THE STRESS TEMF

It is appropriate to begin the account of the properties of the Pt/Au thermocouple with a brief overview of its special characteristics and mode of use as a superior temperature sensor for service in the range 0-1000°C. Figures 1, 2 show immersion-TEMF profiles in freezing Sb and Ag fixed points. Double insertion (I) - withdrawal (W) immersion characteristics in the same freeze are presented to gauge the stability of the elemental thermopowers of the couple over an interval of ~ 4 h. Figure 1B, C, and Fig. 2B trace profiles obtained with the Pt and Au thermoelements welded together as a regular junction sheathed (RJS) thermocouple. In Figs. 1B, and 2A, B

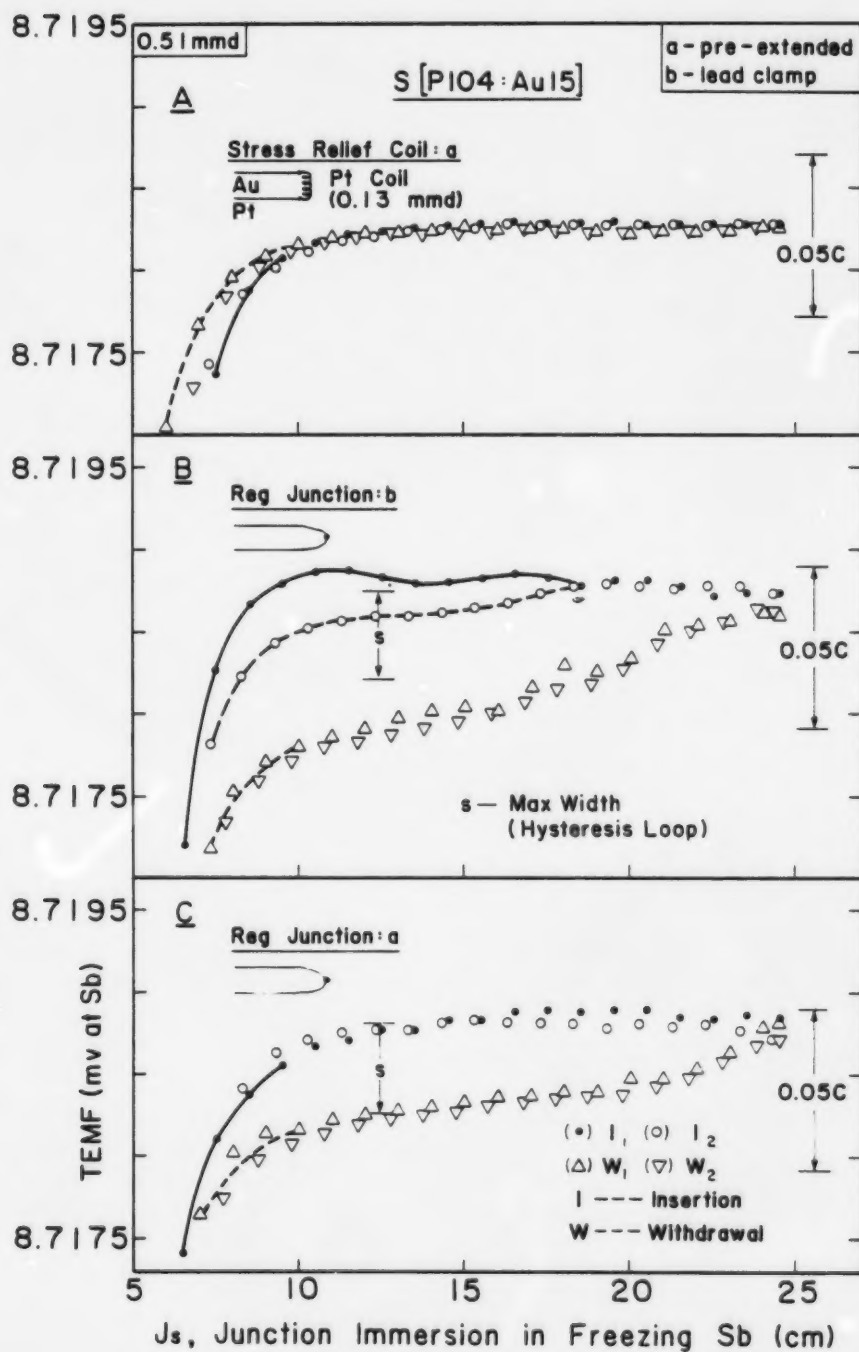


Fig. 1 Immersion characteristics of a Pt/Au thermocouple in freezing Sb: A, stress-relieved junction; B, C normal welded junctions.

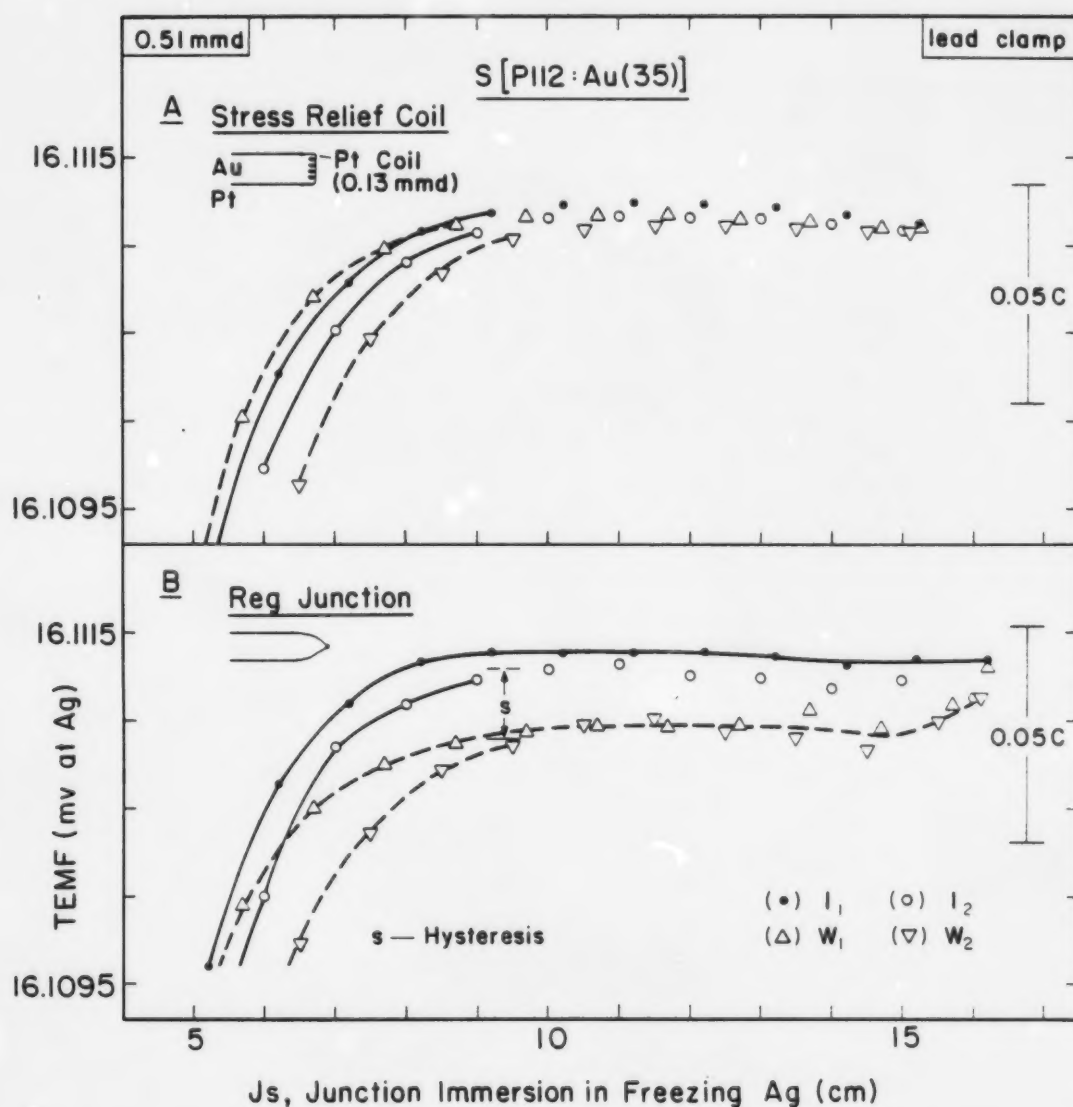


Fig. 2 Immersion characteristic of a Pt/Au thermocouple in freezing Ag: A, stress-relieved junction; B, normal welded junction.

a small bar clamp immediately above the bakelite head [19] of the thermocouple was used to gently compress the insulation against the elements to serve as the tied-down reference from which both elements expanded inside the sheath; in Figs. 1A, C the thermoelements were pre-extended by immersing the couple into the Sb point for 15 min and then removed. Figures 1B, C and Fig. 2B clearly indicate hysteretic loops between the TEMFs generated on insertions and those on withdrawals, with maximum loop-widths amounting to equivalent temperatures of $\sim 0.04^{\circ}\text{C}$ and 0.02°C , respectively, in the Sb and Ag points. The immersion characteristics of the same Pt/Au couple at the Zn, Sn and In points revealed stress-loops having measurable but smaller amplitudes that decreased with the fixed point temperature. Mechanical stress arising from the differential (Au expansion $> 3 \times$ Pt expansion) thermal expansions of the Pt and the Au elements in the furnace gradients introduces an additional stress-TEMF to the normal Seebeck TEMF. The cyclic loop arises because portions of the thermoelements expand on insertion and contract on withdrawal as the couple is progressively inserted or withdrawn into or from the fixed point. Similar but very much larger cyclic stress-induced variations in TEMF (first noted by Morgan [20]) are commonly present on inserting and withdrawing mineral insulated metal sheathed (MIMS) thermocouples that have significant differences in thermal expansions between sheath material and sensing elements; (e.g. in this laboratory loop-widths $\sim 1.5^{\circ}\text{C}$ have been observed on immersion-TEMF profiles in Sb and Ag points with type S MIMS couples sheathed in Inconel).

Figures 1A, 2A show immersion-TEMF profiles determined with the same couples when the two sensing elements were joined together using a $\lesssim 5$ turn stress-relieving coil. Now the multiple insertion-withdrawal TEMFs, at immersions beyond the thermal conduction-loss thresholds vary only the equivalent of $\lesssim 0.01^\circ\text{C}$, which attests both to the high quality of the fixed point realizations and to the high degree of thermoelectric homogeneity in the Pt and Au thermoelements. The stress-relieving coil deforms easily as the Pt and Au elements expand in the furnace gradients and can not transport the differential expansion stress to the portions of the wires in the TEMF-generating temperature gradient zones. Avoidance of the expansion stress removes the stress-induced hysteresis found on the immersion-TEMFs of couples formed with regular welded junctions and allows a Pt/Au couple to reveal (Figs. 1A, 2A) its superior intrinsic thermoelectric homogeneity and to attain nearly the performance level expected of an ideal thermocouple with truly homogeneous elements.

Figure 3 elucidates the nature of the stress-TEMF developed in Au elements. When tension is applied to a long polycrystalline wire it is resolved, under crystallographic restraints, into tensile, compressive, and torsional forces; Fermi levels and therefore thermopowers of such strained wires are slightly altered [21] either reversibly in the elastically deformed region or permanently when plastic deformation occurs. The stress-TEMF is the change in the Seebeck TEMF generated in a temperature gradient by a thermocouple with

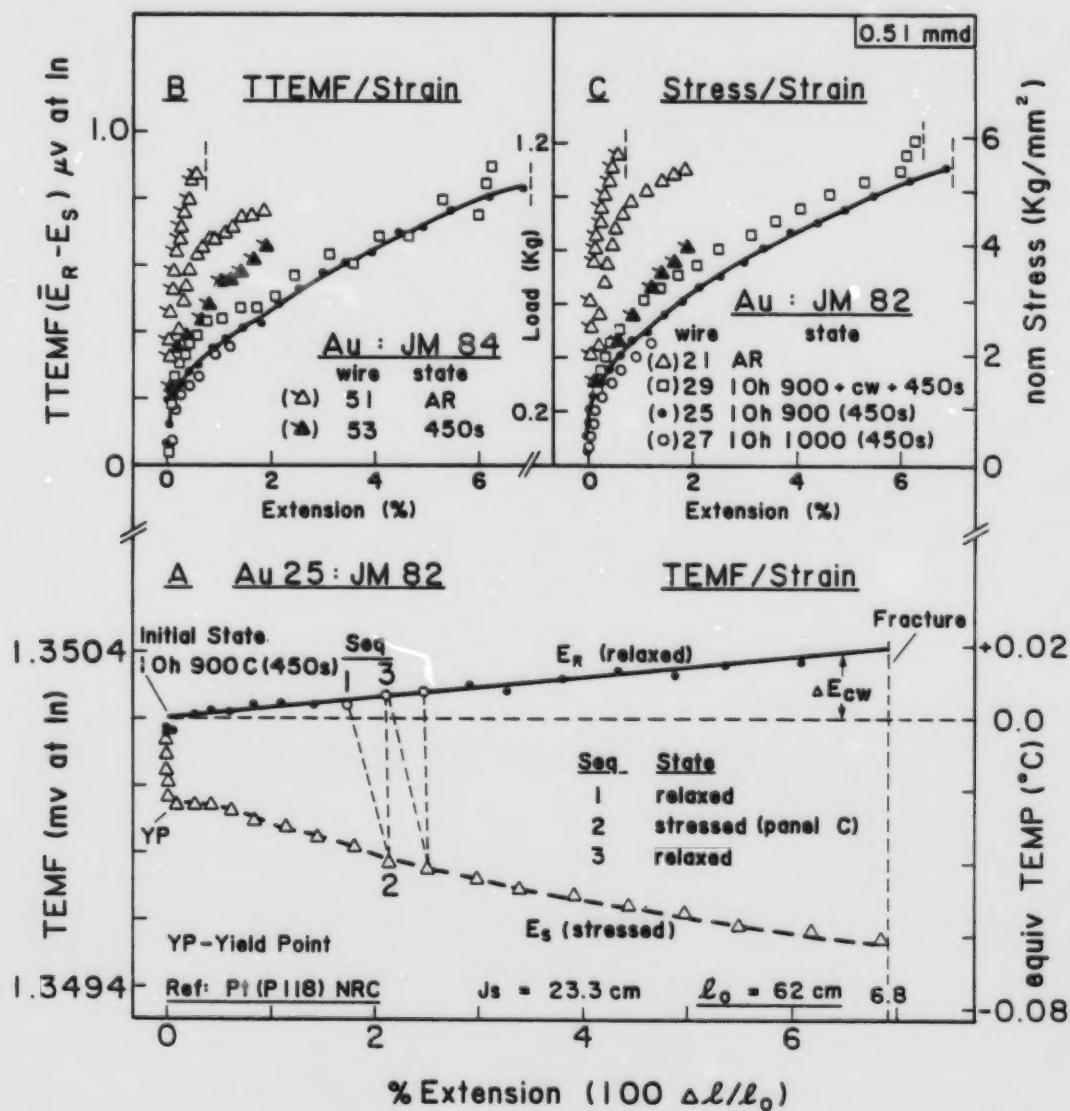


Fig. 3 TEMF(A) and TTEMF(B) generated in a Au thermoelement (Au25) incrementally strained to fracture under increasing tensile stress (C) in the gradient of an In point furnace; B, C include yield point data on other Au wires in a variety of anneal states.

its elements in stressed states to that attained with the elements in relaxed (unstressed) states. Less rigorously, differential expansion on long polycrystalline wires manifests itself most obviously by changes in length and because stress-TEMFs are examined most simply in test-rigs that apply stress along the elemental lengths, we have more commonly labelled the stress-TEMF as the tensile-TEMF (TTEMF).

Figure 3A shows the effects of stressing the Au element on the TEMF generated by a Pt/Au couple in the In point, the reference Pt element being unstressed. (Detailed descriptions of the stressing-rig and the experimental methods used earlier to study stress-TEMFs in Pt and Pt10Rh elements are given in [5]). In brief, a series of cyclic stresses were applied to the Au element with preset, consecutively increasing, maximum loadings with each cycle. Starting in the relaxed state (seq. 1) the stress was uniformly increased to the predetermined maximum (seq. 2), held several seconds to observe and record TEMF, load and displacement, then uniformly decreased (seq. 3) to the unstressed rest position; the duration of each cycle was ~ 1 minute. In Fig. 3A the stressed TEMF decreases (more negative), at first proportionately with strain under elastic deformation until a fairly sharp yield point is reached, and thereafter continues to decrease with increasing inelastic strain until fracture. The relaxed TEMF, after yielding, appears to increase (more positive) slightly till fracture implying, most probably, a change arising from a measurable strain-hardening in the deformed Au element. Figure 3B plots the yield TTEMFs and Fig. 3C the yield stresses against strains that were determined on element Au25

shown in Fig. 3A but, to broaden the view, information on other Au elements prepared in a variety of preannealed states is included. Clearly as-received (AR) wires have higher yield TTEMFs and stresses than wires preannealed at high temperature. Element Au29, prepared with an initial 10 h 900°C (450s) anneal, then cold-worked (CW) by coiling and uncoiling four times (4X cuc, 1.7% ext., [5]) and given a finishing overnight sheath anneal at 450°C, has measurably larger yield TTEMFs and stresses than element Au25 prepared with the same preanneal but not cold-worked; the final 450°C anneal does not remove all the defects introduced during the cuc deformations.

Further, Figures 4A, C show the yield TTEMFs and stresses that were measured when a Au element, preannealed at high temperature, was successively yielded at the progressively higher temperatures in the In, Sn, Zn and Sb points; the yield points are relatively sharp and easily determined. Figures 4B, D plot the variations with temperature of the yield TTEMFs and stresses deduced for element Au27 and also those from an earlier study [5] on a representative 0.5 mm annealed Pt wire. The temperature variations of the yield TTEMFs and stresses are similar in form for the Au and Pt thermoelements but the magnitudes are substantially larger for the Pt wire.

The stress-TEMP loops shown in Figs. 1B, C result from the sum of the stress-TEMPs generated in the Sb furnace temperature gradient by differential thermal expansions along both the Pt and Au elements in a Pt/Au couple of regular construction. It is fortunate that the differential expansion stresses and degrading stress-TEMPs can

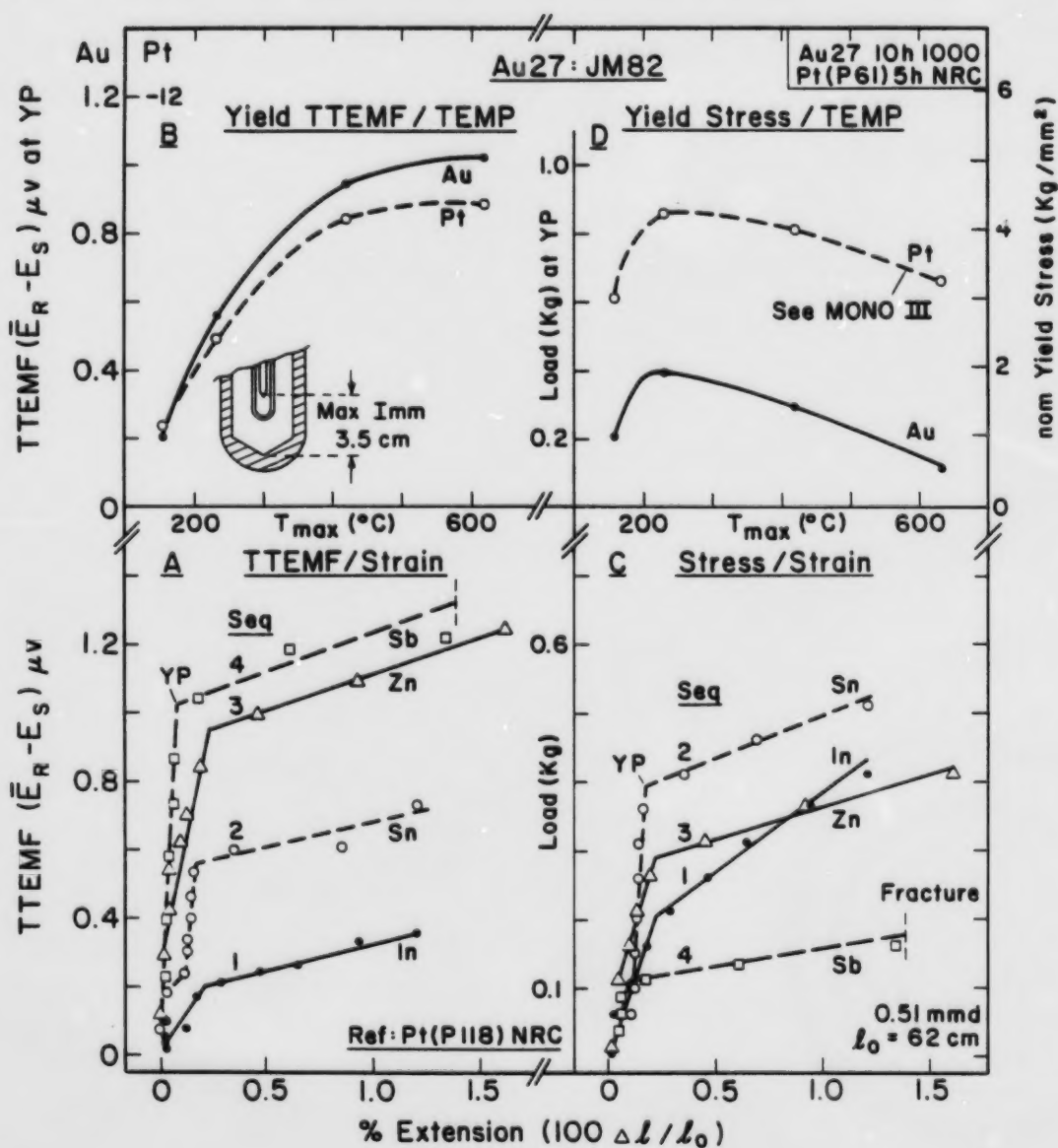


Fig. 4 Yielding curves A, C; and variations of yield points with temperature B, D, for a Au wire preannealed for 10 h at 1000°C and for comparison, an NRC-annealed Pt wire.

be reduced to negligible amounts (Fig. 1A) simply by using a weak stress-relief coil to form the junction between the Pt and the Au elements. Consequently, the junctions of Pt/Au couples intended for precise temperature measurements, at temperatures greater than ambient, should always be fabricated using stress-relieving coils. For convenience here normally sheathed (S) couples using such stress relieving junctions (SRJ) are identified as SRJS thermocouples; it is also customary to use the lead clamp to restrict undesired travel of the elements in their insulating lead channels.

PERFORMANCE AT THE FIXED POINTS

a) ICE REFERENCE POINT

Figures 1A, 2A clearly indicate that the nominal precision attainable with an adequately immersed Pt/Au couple in temperature measurements in the Sb and Ag points approaches $\pm 0.01^{\circ}\text{C}$. This performance is due largely to the thermoelectric stability and homogeneity of the hot junction segments of the Pt and Au elements. To realize the highest possible measurement precision, however, care must also be exercised to ensure that the ice reference junctions are immersed sufficiently to attain thermal equilibrium at the ice point, and that unwanted systematic TEMFs arising from chemical and defect inhomogeneities along portions of either the thermoelements or the two copper potentiometric leads in the ice to room temperature gradient are not included in the TEMF measurements.

The NRC ice point arrangement and practices have been described [3] with details of the performance of the ice reference junctions of the Pt/Pt10Rh couple. Using similar techniques, Fig. 5 shows representative examples of the immersion characteristics of the ice reference junctions of a Pt/Au couple. The hot junction of a regular sheathed couple, immersed 47 cm ($\gg$ lead conduction-loss threshold immersion) in a long ice point cell, here serves as the reference junction at the ice temperature as the two regular ice reference junctions (and pyrex lead wells) are withdrawn from a regular ice reference cell. E_s is the difference in TEMF between the properly immersed hot junction and the ice reference junctions at immersion J_s ; E_o is the small residual emf in the measuring circuit when the three thermocouple junctions were immersed at depths greater than their thermal conduction-loss thresholds; $E_s - E_o$, therefore, is a measure of the thermal conduction-loss error in the TEMF measurement at ice reference junction immersion, J_s . The immersion characteristics of the ice reference junctions of this Pt/Au couple are similar to the corresponding ones measured with Pt/Pt10Rh couples because the thermal conduction losses in the Cu conductors dominate. To reduce this conduction error to less than the equivalent of a few mK in a TEMF measurement at the Ag point, Fig. 5 shows that the ice reference junctions of this couple, using (0.32, 0.51) mm Cu potentiometric leads, respectively, should be immersed ($\gtrsim$ 14, 18) cm in dry wells and ($\gtrsim$ 10, 8) cm in wet wells. The normal practice in our laboratory is to

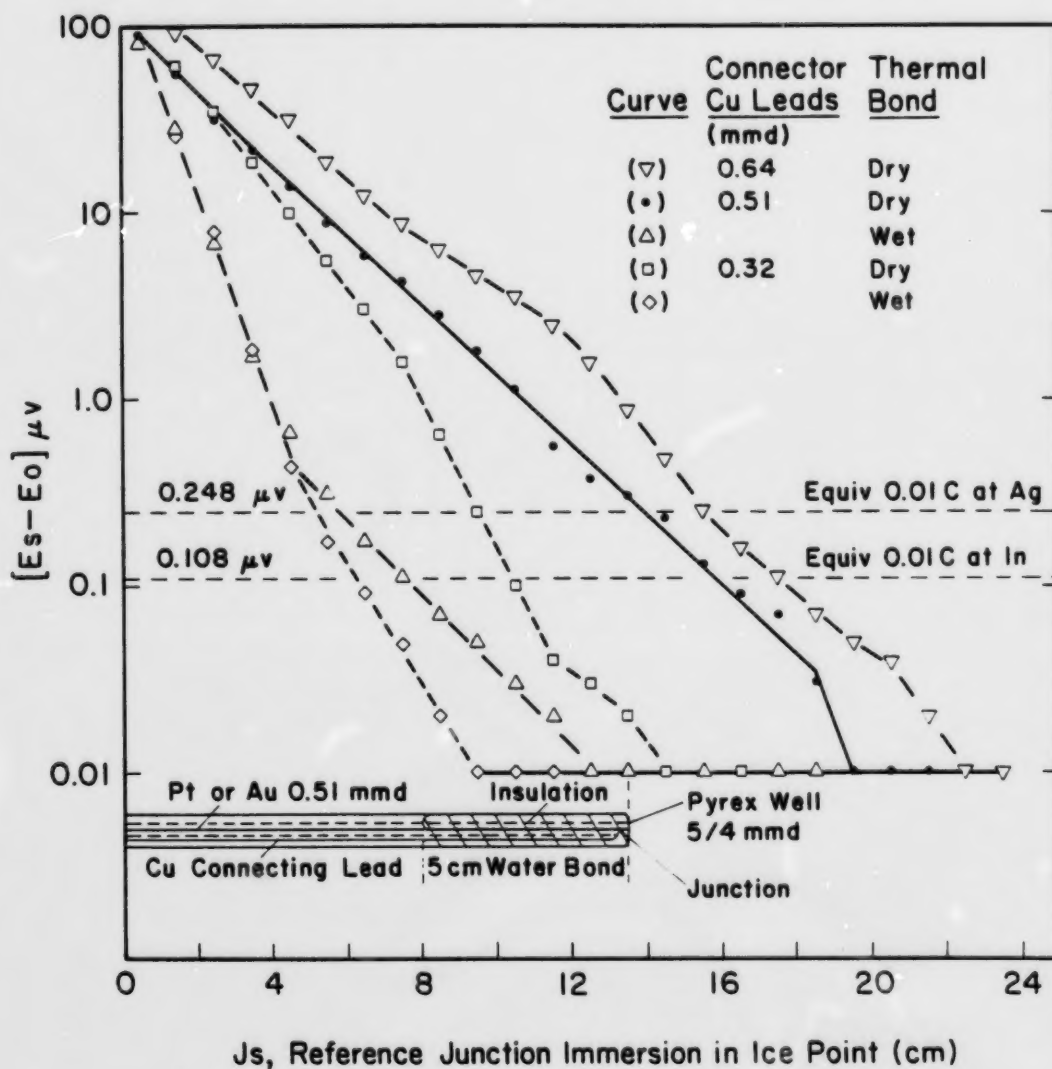


Fig. 5 Immersion characteristics of Pt/Au ice reference junctions.

use 24 cm immersions for thermocouple ice reference junctions which substantially exceed these measured conduction-loss thresholds. In research service, where the thermoelements may be frequently withdrawn from sheaths and lead harnesses for special heat treatments and reanneals, dry wells are normally used to avoid moisture problems with the electrical insulations.

Since TEMF measurements at fixed points with the Pt/Au couple may be made reliably to better than $0.1 \mu\text{v}$, additional care is needed to ensure that (1) the lengths of the Pt and Au elements exposed to the ice to room temperature gradient are maintained in strain-annealed and thermoelectrically homogeneous states, and (2) that the two Cu potentiometric leads are also strain-annealed, homogeneous and thermoelectrically equivalent. The regular preparatory anneals place Pt and Au elements in satisfactory annealed states. Early in this study, however, measurable thermoelectric differences were noted between various batches of Cu wire in both as-received and annealed states. As a consequence, ASTM type TP copper wire was selected for use as the potentiometric leads with the Pt/Au couple; the portions of the two Cu wires that are exposed to the ice to room temperature gradient are preannealed overnight in argon at 450°C .

Figure 6 illustrates how strain in one of the Cu potentiometric leads of a Pt/Au couple may effect the ice reference junction immersion-TEMF errors in the ice point and could introduce a significant systematic error in a TEMF measurement at the Ag point.

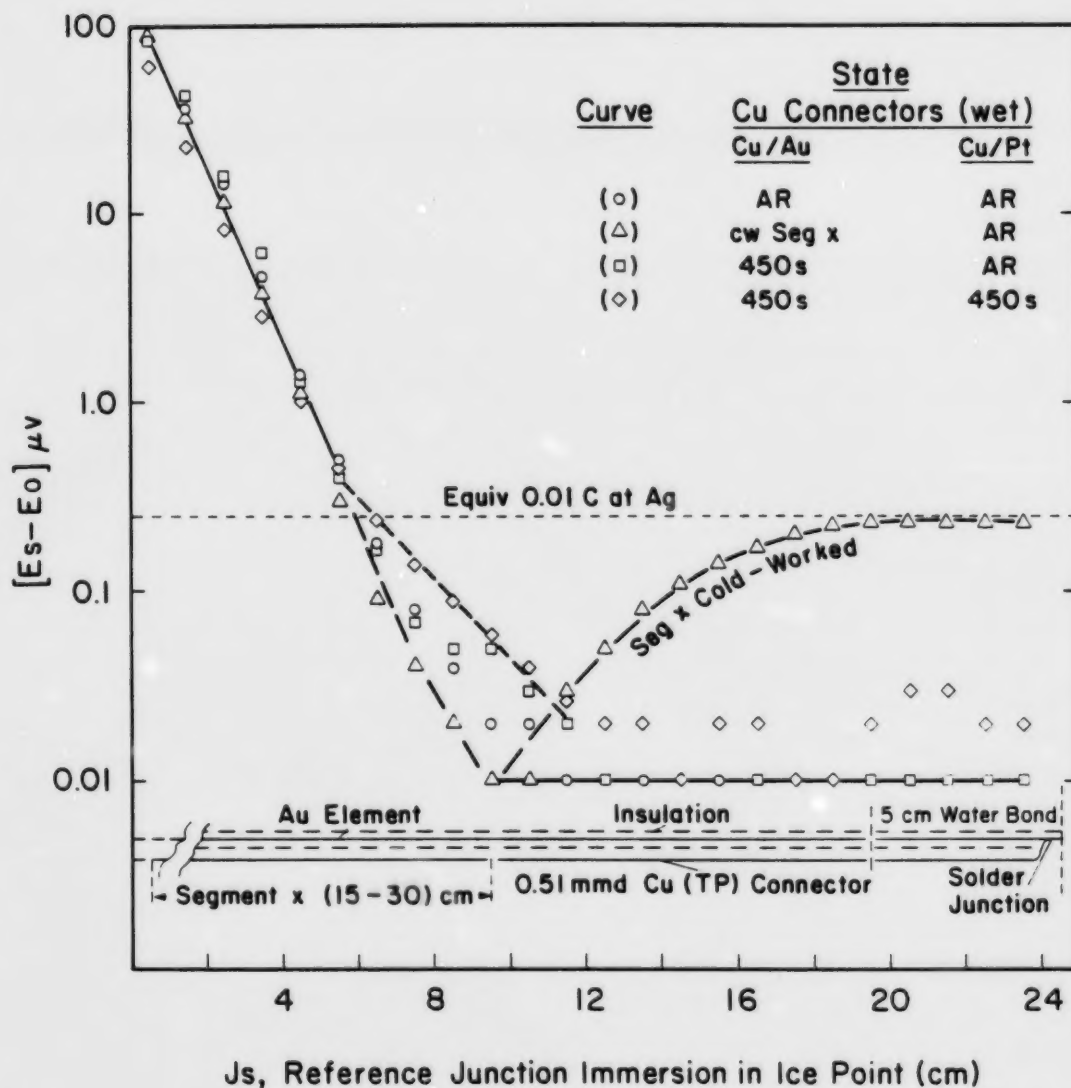


Fig. 6 Effect of the anneal state of the Cu potential leads on the immersion characteristics of Pt/Au ice reference junctions.

Immersion characteristics are shown with the two Cu (TP) potentiometric leads in various annealed states: AR, as-received; 450s, annealed in argon overnight at 450°C; cw, segment x cold-worked. Segment x of the Cu lead connected to the Au element was the portion of the Cu lead which, at full immersion, was exposed to the ice to room temperature gradient, and included the length of this element most susceptible to bending or kinking during normal manipulations of the lead harness. This segment was cold worked by gently coiling and uncoiling 10 times (10X cuc) the 15 cm length of wire around a 10 mmd silica tube under a bending load of 165 g. The immersion characteristic of the ice reference junctions when one Cu lead was strained is clearly altered from those obtained when the two Cu leads were more nearly matched and thermoelectrically equal; at maximum immersion this ice reference junction error appeared stable and amounted to $\sim 0.25 \mu\text{v}$. Reannealing the strained conductor essentially removed the strain-TEMP error.

To sum up, this brief study shows that disciplined care in ice point realizations, and verifications of adequate immersions of and thermoelectric homogeneities along both the thermoelements and the Cu connectors in the ice reference junctions, are required to eliminate systematic but unnecessary uncertainties in high precision TEMP measurements that are intended to exploit the full capability of the Pt/Au couple.

b) METAL FIXED POINTS

In this section an overview of the general performance of the Pt/Au thermocouple in the determination of both time-TEMF and immersion-TEMF curves during freezing and melting transformations in high purity Zn, Sb and Ag metal fixed points will be given for two reasons: (1) the ultimate measure of the thermoelectric homogeneity along the elements of a thermocouple deduced from the immersion-TEMF curves in high purity metal fixed points is directly dependent on the quality of the fixed point realizations and; (2) a comparison of the transformation curves and the immersion characteristics determined with the Pt/Au couple to corresponding ones determined with the high temperature platinum resistance thermometer provides extra parameters that are valuable in appraising the merits of both types of sensor.

Figure 7 presents time-temperature curves determined with a Pt/Au [Pt(P109):Au31] couple during freezing and melting of Zn and Sb ingots of nominal 59 grade purity. Using conventional nucleation techniques and transformation durations of several hours, the slow induced freeze (SIF) on Zn, the outside nucleated slow induced freeze (ONSIF) on Sb, and the melting curves determined after slow freezing reveal alloy freezing and melting ranges of a few mK for the 59 grade metals. These transformation ranges are entirely consistent with corresponding alloy freezing and melting ranges measured earlier [22, 23] using platinum resistance thermometry. In addition, the liquidus breaks on the melting curves agree closely with the highest liquidus points measured following recalescence on the preceding freeze which

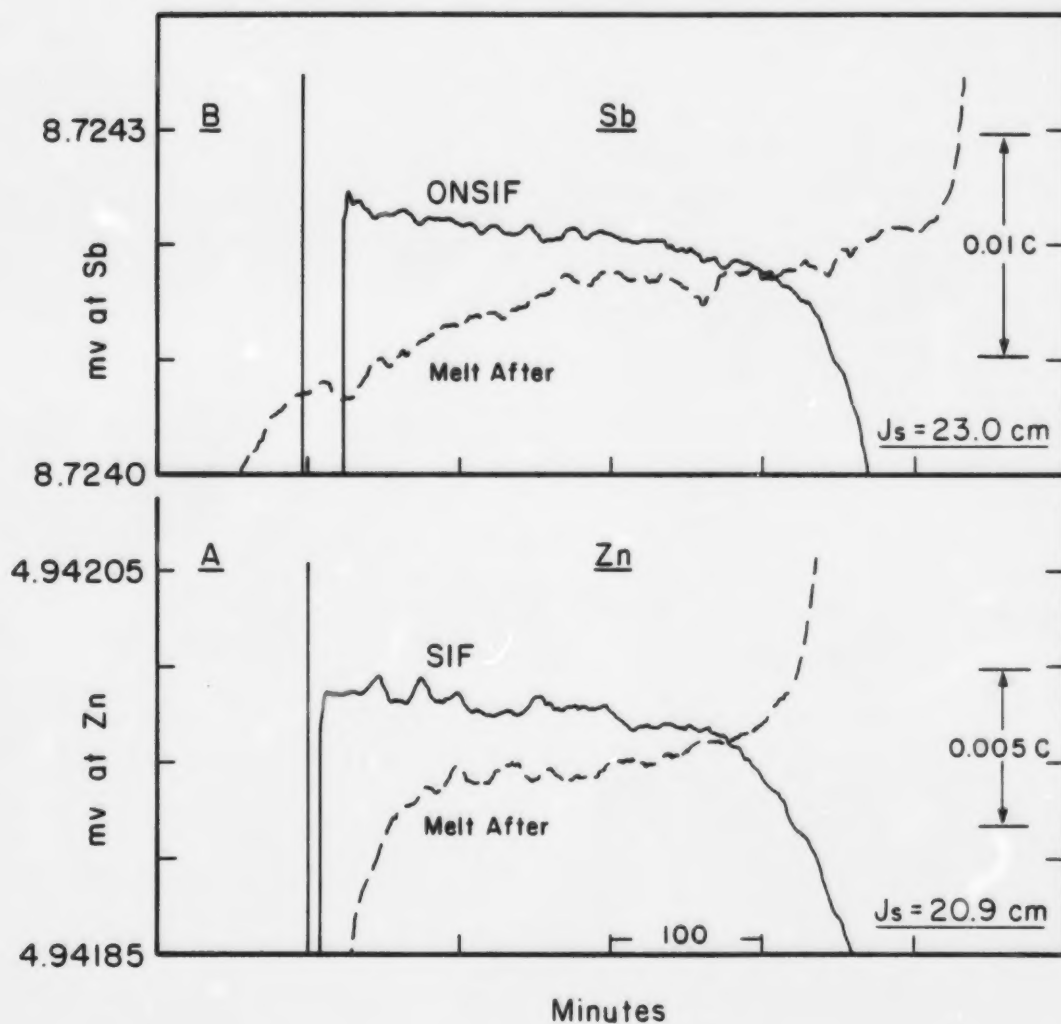


Fig. 7 Typical freezing and remelting curves in high purity Zn and Sb determined with a Pt/Au thermocouple.

indicates satisfactory thermal equilibrations of the temperature sensor to the transforming ingots. The small (equiv. < 1 mK) fluctuating variations in TEMF observed along these transformation curves are attributed to instrumental fluctuations in the output of the DVM and not to fluctuations in ingot temperatures; variations of these magnitudes are not observed with conventional D.C. resistance measurements.

Figure 8 presents a selection of Ag thermal curves measured with a variety of nucleating techniques and transformation rates; with the exception of the two curves in panel D, these transformation curves were determined on 69 grade Ag (Ag.3). Figure 8A shows an outside nucleated slow freezing (ONSF5) curve and the subsequent remelting curve. The nucleating technique used in this laboratory for the high temperature fixed points (Ag, Cu, AgCu eutectic) is similar to that used with deep supercooling melts like Sn [24] and Sb [23]: in such cases it is desirable to achieve the nucleation of solid phase in thin shells on the walls of the crucibles and at the same time keep the furnace blocks at temperatures close to the liquidus points of the freezing metals in order that the solidifying ingots do not have to supply large amounts of latent heat to reheat the undercooled furnace blocks which would substantially degrade the freezing point realizations. The ONSF5 nucleation uses an interval of 5 seconds from beginning the withdrawal of the ingot completely free of the furnace into the room temperature zone to the beginning of reinsertion. At high temperatures, short periods of radiation loss to the room quickly

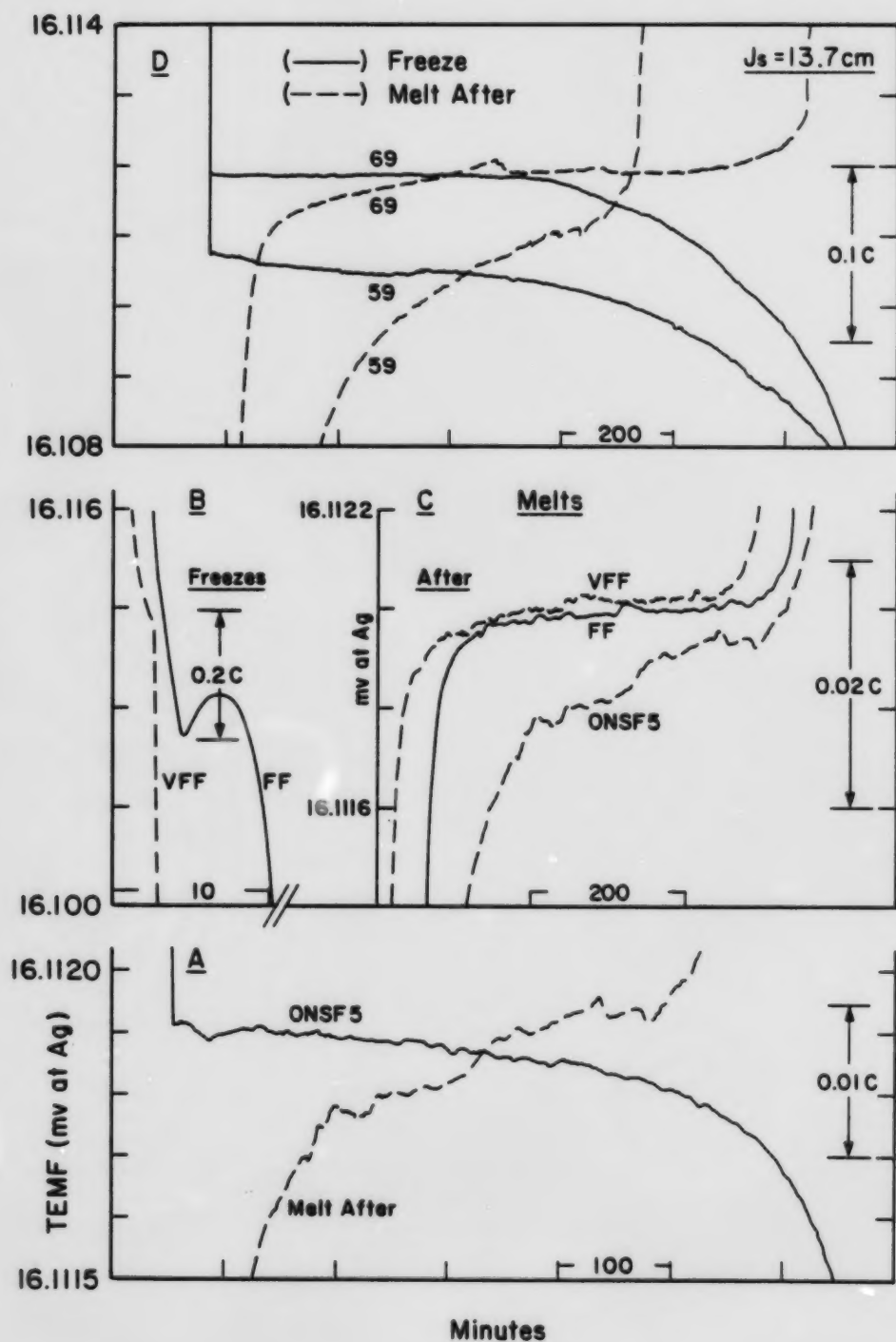


Fig. 8 Typical freezing and remelting curves in high purity Ag determined with a Pt/Au thermocouple.

chill the crucible walls and initiates the desired solid nucleation without solidifying an excessive fraction of the ingot. (Protective face shields, gloves and aprons should be used during the manipulations used for outside nucleation procedures on high temperature fixed points).

Thermal analyses at the Ag point provide the means to critically assess both the performance of the Pt/Au [Pt(P111):Au33] couple as a precise temperature sensor and the quality of the fixed point realization at a temperature near the upper temperature limit of the thermocouple. Figure 8A shows that the overall alloy freezing range of the 69 grade Ag (Ag.3) in the slow (10 h) freeze was $< 0.01^{\circ}\text{C}$ and that over half the solidification time was spent in a temperature range of 2 mK. Remelting after the slow freeze shows an overall alloy melting range of $< 0.01^{\circ}\text{C}$ with the liquidus break on the melting curve a few mK higher than the highest (plateau) liquidus temperatures observed on the preceding freeze.

The effects of freezing rates on the shapes of the freezing and remelting curves are illustrated in Fig. 8B, C. Very rapid solidification curves are shown in Fig. 8B: for the very fast freeze (VFF), the ingot was withdrawn from the furnace and completely solidified in room air; for the fast freeze (FF), the ingot was withdrawn into the room air for 1 min and then reinserted into the furnace; at these freezing rates, the sensor can not be in thermal equilibrium with, and therefore lags, the ingot freezing temperatures. Although very rapid freezes are of limited use in examining the

properties of either sensor or fixed point, the difference in the melting ranges of an ingot after rapid and very slow freezing gives important information on the purity of a sample. After rapid freezing [25, 3] the impurity solutes are micro-segregated fairly uniformly throughout the ingot in and around small grains and dendritic substructures; after very slow freezing the solutes are nearly radially segregated in columnar grains from crucible-wall to thermometer-well, the segregation dependent on the solid-liquid distribution coefficients of the solute and the grain size on the rate of freezing. As a consequence of these solute segregation differences, melting ranges measured following rapid solidifications are narrower than those measured after slow freezing; for our 69 grade Ag (Ag.3), Fig. 8C indicates melting ranges of $\sim 0.01^{\circ}\text{C}$ and 0.003°C , respectively, following slow and rapid freezing. For purer Ag samples such melting range differences would be smaller and the liquidus breaks on the melting curves would more closely approach the liquidus point determined on the slow freezing curve.

Finally, Fig. 8D compares slow freezing and remelting curves determined on 69 (Ag.3) and 59 (Ag.2) grade Ag ingots to illustrate the ready capability of the Pt/Au couple to distinguish among samples of high purity Ag. The liquidus point of Ag.2 is $\sim 0.05^{\circ}\text{C}$ lower than that of Ag.3 and its nominal melting range after slow freezing is estimated to be $\sim 0.3^{\circ}\text{C}$. Earlier studies [3] on rapidly solidified 59 grade Ag (Ag.1) revealed overall melting ranges of $\sim 0.1^{\circ}\text{C}$. The sensitivity of the Pt/Au couple is clearly adequate for selecting the purest Ag

samples using criteria based on accurate comparisons of both liquidus points and alloy melting ranges following slow and rapid solidifications. Liquidus point comparisons may be carried out with a precision of a few mK. Figure 8C shows that measurable differences in melting range following rapid and slow freezing, due to differences in impurity segregations, are found on even a 69 grade Ag ingot; substantially purer Ag would be required before melting curves after both slow and rapid Ag freezes would coincide.

The immersion-TEMF characteristics of a thermocouple in the fixed points during phase transformations provide additional and even more stringent tests of both the sensor and the fixed point realizations by revealing basic information on the thermoelectric homogeneity along the thermoelements as well as the temperature stability of, and gradient in, the fixed point during transformation. Figure 9 shows insertion-withdrawal characteristics of a Pt/Au couple during single slow freezing and remelting in both Sb and Ag fixed points. The IWIW characteristics were determined over a period of ~ 4 h on slow freezes beginning ~ 30 min after nucleation, which period, the earlier work (Figs. 7B, 8A) had shown, encompassed the highest and narrowest (plateau) range of freezing temperatures. On slow melting the immersion characteristics were also measured over a period of ~ 4 h, beginning ~ 1 h after the primary arrest when melting temperatures were within 0.01°C of the liquidus point attained on the prior freeze. A separate working Pt/Au couple was used to monitor temperature during the initiations of the phase transformations. In Fig. 9 the immersion

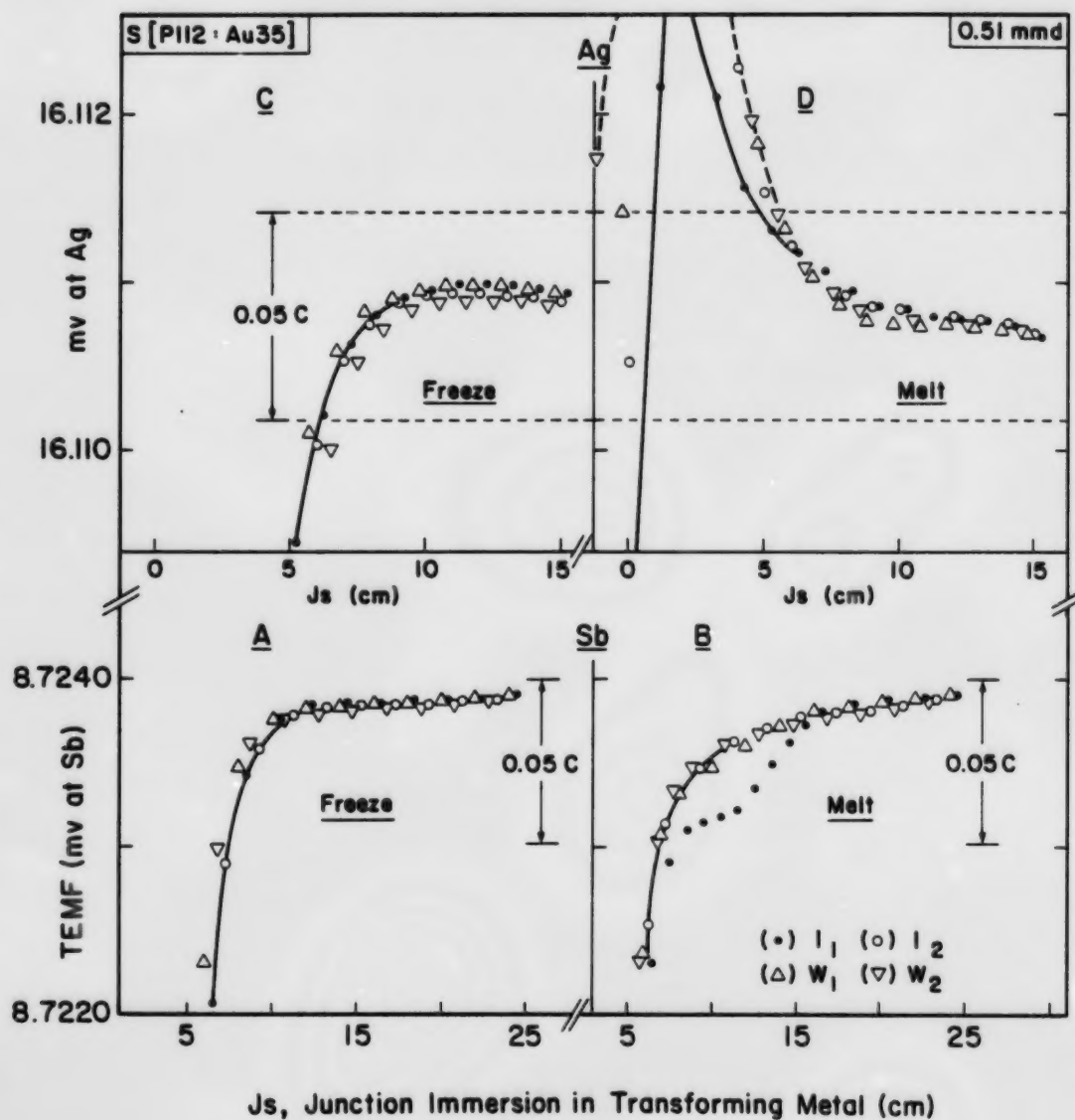


Fig. 9 Multiple insertion-withdrawal immersion characteristics on freezing and remelting high purity Sb and Ag determined with a Pt/Au thermocouple.

characteristics during freezing and melting are placed side by side to facilitate direct comparisons of the transformation temperatures in the ingot.

On the freezes, at immersions greater than the conduction-loss thresholds, temperatures remain stable to within 0.01°C during the two IW probings. This indicates high thermoelectric homogeneity in the thermoelements, a proper control of the freezing temperatures by the freezing interface in the transforming pure metal, and good regulation and control of the fixed point furnace power during the transformation. The conduction-loss thresholds for this couple are 10 and 8 cms, respectively, in these Sb and Ag fixed points.

On the melting profiles, at deep immersions, the temperatures at fixed immersion also appear stable to $< 0.01^{\circ}\text{C}$ over the long measuring interval. At maximum immersion in the Sb point no measurable difference ($> \pm 1 \text{ mK}$) was observed (Figs. 9A, 9B) between freezing and melting temperature; in the Ag point at maximum immersion the melting temperature was 11 mK (Fig. 9D) lower than the corresponding freezing temperature.

At immersions less than the thermal conduction thresholds temperature variations are observed that arise primarily from the difference in the ingot morphology during melting from that during freezing. On melting Sb (Fig. 9B) the profile at shallow immersions on the 1st insertion (I_1) track out a small step that is probably due to the melting of pockets of alloy enriched in segregated impurity having distribution coefficients < 1 . Thereafter, the $W_1 I_2 W_2$ profiles, similar to the repeated profiles on the prior freeze (Fig. 9A), nearly

coincide. Between conduction threshold and maximum immersion, temperature ranges of 12 mK and 8 mK, respectively, were measured from these melting and freezing immersion profiles. In melting Ag, Fig. 9D clearly shows a gross thermal spike (amplitude < 0.3 K above liquidus point) on entrance immersions of the sensor into the melt; the spike arises from thermal conduction down the thermocouple to the junction, excess heat being supplied by the top furnace-block heater. Notwithstanding the slightly unbalanced furnace block during melting, these immersion profiles indicate a thermal conduction threshold during melting of 8 cm similar to that observed on the freezing profiles when the furnace block temperature gradient was adjusted to $\sim \pm 0.1$ K over 20 cm.

The thermal analyses in Figs. 7-9 show that the Pt/Au couple possesses the intrinsic stability and sensitivity for critical appraisals of fixed point realizations to a precision of $\lesssim 10$ mK.

As a further illustration, Fig. 10 presents the variations in freezing temperatures that were measured by changing the pressure of the inert gas over Sb, AgCu, and Ag freezing point cells; temperature changes well inside 10 mK are delineated. In Fig. 10, the freezing temperatures of Ag and Sb increase 8 and 1 mK/atm, respectively in good agreement with measurements using platinum resistance thermometry; ~ 6 mK/atm determined on Ag freezes by Bongiovanni et al [26] and Xumo et al [10], and 0.85 mK/atm observed [25] by ourselves on freezing Sb. A Clausius-Clapeyron calculation of the pressure coefficient of Ag using

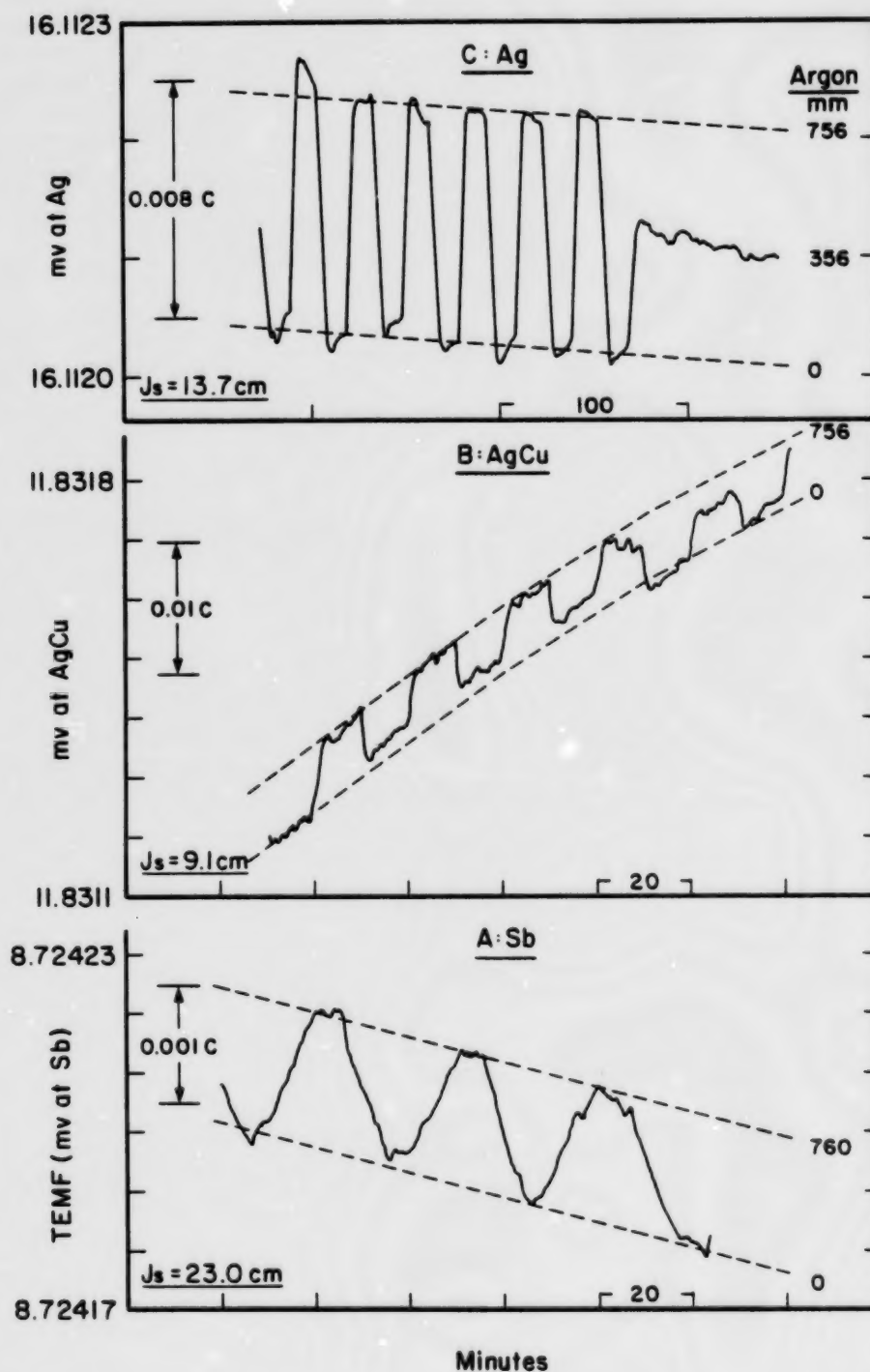


Fig. 10 Effect of external gas pressure on the freezing points of Sb, AgCu eutectic and Ag determined with Pt/Au couples: A, B [Pt(109):Au31], C [Pt(111):Au33].

specific volumes of liquid and solid at the freezing temperature of 11.58 [27] and 10.95 [28] cc/mole, respectively, and 2700 cal/mole [29] for the heat of fusion yields a value 7.0 mK/atm. For the AgCu eutectic a variation of $\lesssim 5$ mK/atm is indicated in Fig. 10B. This value is less accurate than those for Ag and Sb because the axial freezing temperatures in the binary eutectic are not nearly as stable or uniform as the plateau temperatures developed on the freezing curves of the pure metals, a consequence of the more complex morphology of the solidifying eutectic (3 phases) as compared with that of the simple two phase transformation of a pure metal.

c) UNIT COUPLE AND ITS INDIVIDUAL ELEMENTS AT THE FIXED POINTS

A comparison of the performance of the Pt/Au thermocouple with that of its individual elements in the fixed points was carried out to further elucidate its properties. The immersion-TEMP characteristics at the fixed points for both the unit couple and its individual elements provide intrinsic information on two important properties — thermoelectric homogeneities and conduction-loss thresholds. In addition, the immersion characteristic of the unit couple is, in principle, equal to the sum of the immersion-TEMP characteristics of its individual elements.

In this section the performance of two Pt/Au couples are examined at the Sn, Zn, Sb and Ag points; one couple [P114:Au45] with 0.51 mm elements and the other [P118:Au30] with a 0.51 mm Pt [P118]

and a 0.25 mm Au [Au30] element. The unit couples were fabricated as regular SRJS couples but the withdrawal characteristics of the individual elements were made separately in type MJ-1 movable junction couples using special sheaths and lead arrangements [19]. In this MJ-1 research couple one element is movable and may be withdrawn from deep immersion in a fixed point while the other element of the couple remains stationary at maximum immersion and serves as the reference element. A weak (0.13 mm, yield point $< 0.2 \text{ kg/mm}^2$) extendable coil of the same material as the reference element joins the movable element to the reference element and is stretched along a flattened section of the sheath as the withdrawal proceeds.

Single IW immersion-TEMF characteristics were determined with the two unit couples at each fixed point. Then the elements were removed and, in succession, mounted first, in a Pt-movable type MJ-1 couple and second, in a Au-movable MJ-1 couple to determine the immersion characteristics of the two Pt and two Au elements, respectively, at each fixed point; in all cases the companion element of the particular unit couple served as the reference in the respective MJ-1 couple.

Figures 11, 12, 13, 14 show the immersion-TEMF profiles of the two couples and their separate elements at the Sn, Zn, Sb, and Ag points. Panels A, C in these figures chart the IW characteristics of the unit couples and panels B, D the withdrawal characteristics of the individual Pt and Au elements. Panels A, C also show the composite immersion profiles derived by summing the appropriate paired individual

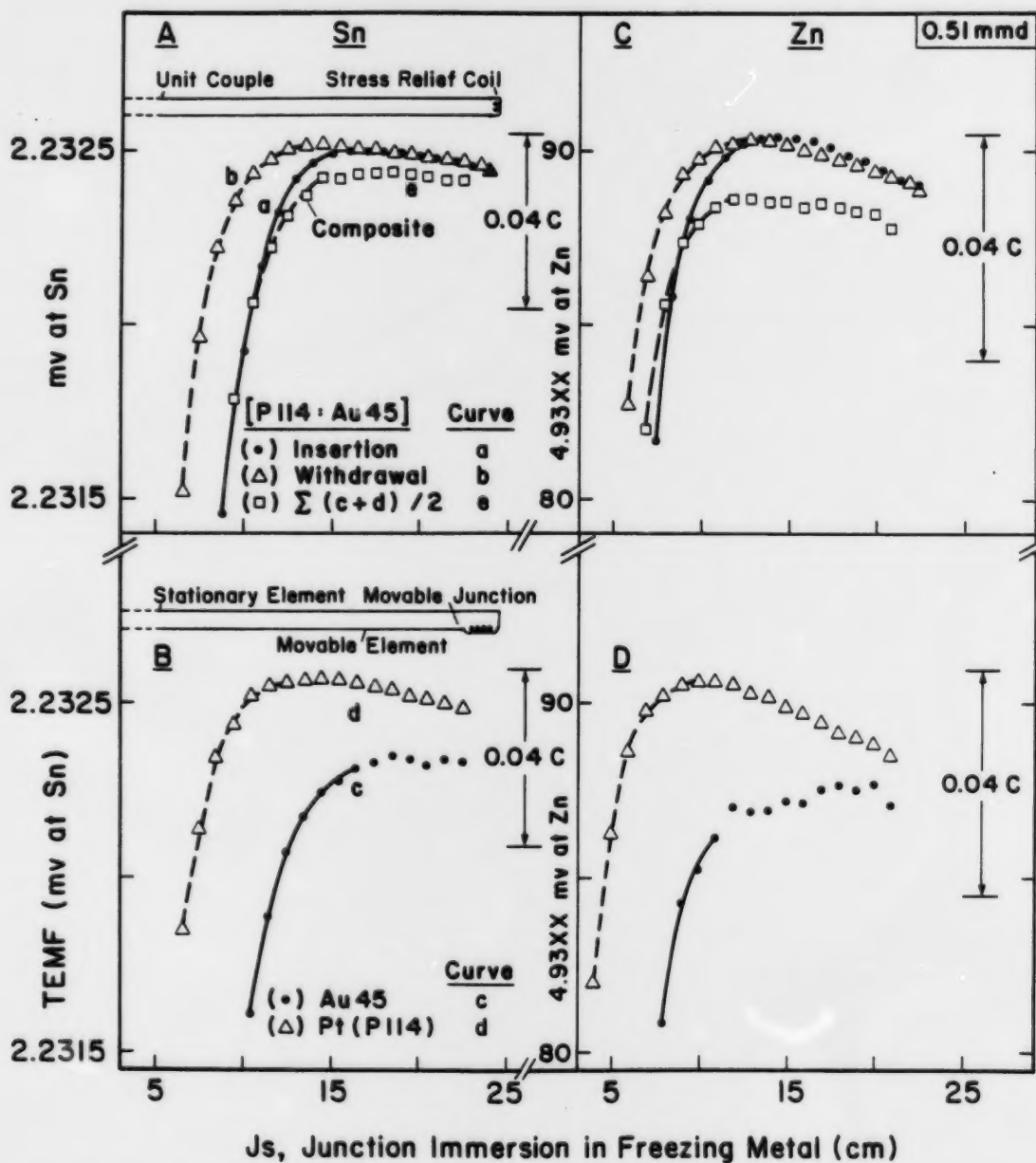


Fig. 11 Immersion characteristics of a unit couple and its individual elements (0.51 mm Pt, Au) in the Sn and Zn points.

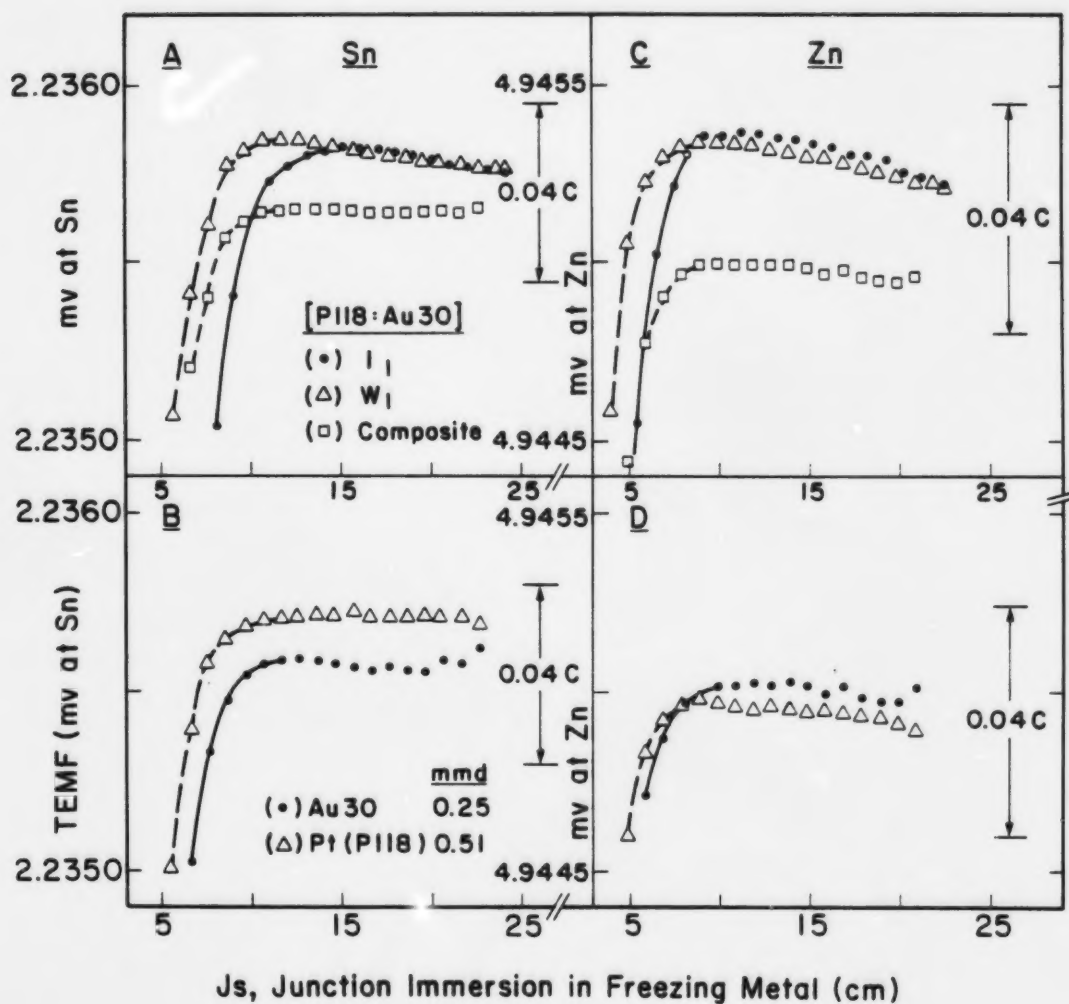


Fig. 12 Immersion characteristics of a unit couple and its individual elements (0.51 mm Pt, 0.25 mm Au) in the Sn and Zn points.

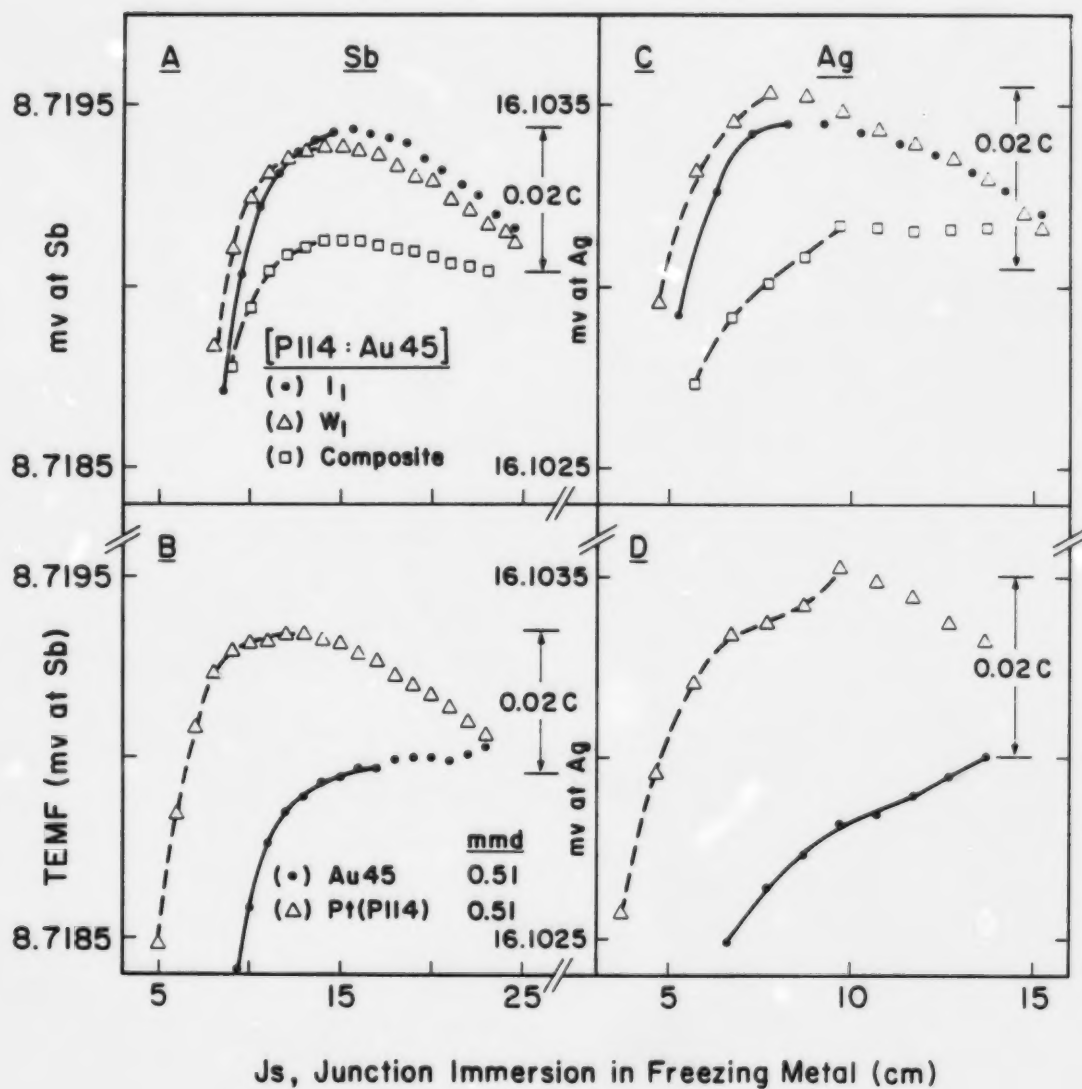


Fig. 13 Immersion characteristics of a unit couple and its individual elements (0.51 mm Pt, Au) in the Sb and Ag points.

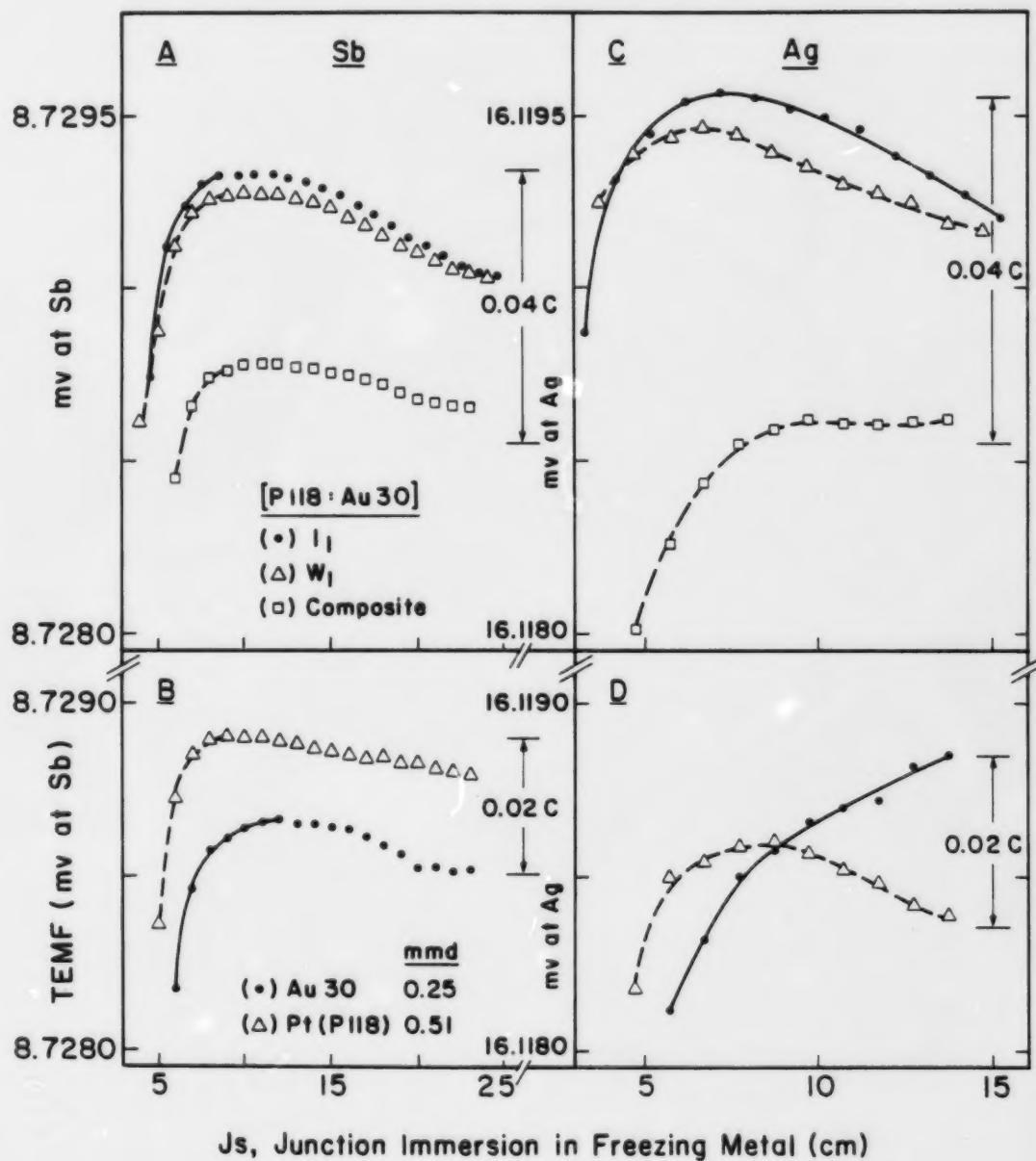


Fig. 14 Immersion characteristics of a unit couple and its individual elements (0.51 mmd Pt, 0.25 mmd Au) in the Sb and Ag points.

immersion characteristics. Both low and high temperature fixed points were used to show how lead conduction-loss thresholds alter with temperature as the proportion of heat supplied to the thermoelements changes from predominately thermal conduction at lower temperatures to radiative transfer at higher temperatures. The 0.25 mm Au (Au30) wire was included to illustrate how a simple reduction in wire size from 0.51 mm Au (Au45) reduces the heat loss down the highly conducting Au lead and effects significant reductions in the threshold immersions for heat loss.

These figures allow estimates (Table I) of the conduction-loss threshold immersions, the overall thermoelectric inhomogeneities along the elements, and the maximum differences between the composite immersion-TEMFs and those measured with the elements combined as regular couples. The variations in the thermal conduction thresholds of the two couples and their separate elements are in accord with general expectations: greater immersions are required for Au elements than for Pt elements of the same diameter; minimum immersion thresholds for separate Au wires and for couples using Au wire [i.e. Pt18:Au30] are measurably decreased when the Au wire size is decreased. The nominal thermoelectric inhomogeneities measured at immersions exceeding the conduction thresholds varied from the equivalent of a few mK at the Sn point to $\lesssim 17$ mK in the Sb and Ag points. The systematic differences of equivalent temperatures of the combined individual element TEMFs from the directly measured values are most probably due to failure of the individual movable elements in the MJ-1 sheaths to

Table I: Measurement parameters of unit couples and individual elements at the fixed points.

<u>Couple/Element*</u>	<u>Fixed Point</u>			
	<u>Sn</u>	<u>Zn</u>	<u>Sb</u>	<u>Ag</u>
Conduction-loss Threshold Immersion (cm)				
P114 : Au45	15	12	12	8
P118 : Au30	11	9	8	6
P114	12	9	8	7
P118	11	8	7	6
Au45	16	12	14	10
Au30	10	9	8	7
Thermoelectric Inhomogeneity (equiv. mK)				
P114 : Au45	6	8	17	16
P118 : Au30	6	8	16	15
P114	6	14	15	9
P118	2	6	6	9
Au45	3	6	4	7
Au30	5	4	7	14
Min. Difference [unit-composite] (equiv. mK)				
P114 : Au45	4	9	8	5
P118 : Au30	13	17	20	24
Max. Difference [unit-composite] (equiv. mK)				
P114 : Au45	6	10	13	14
P118 : Au30	15	22	27	37

* P114, P118, Au45 - 0.51 mm; Au30 - 0.25 mm

attain true thermal equilibration with the fixed points. In the MJ-1 couple the sheath is flattened along 25 cm from the tip to allow space to accommodate the extendable coil. As the withdrawal proceeds the movable element (with low emissivity) is not confined and occasionally contacting the bore wall of the sheath and therefore is more isolated from the fixed point temperature than in a regular sheath. As a consequence, the differences between the combined individual TEMFs and those of the corresponding unit couples at the fixed points are twice as large for the couple with the 0.25 mm Au element as for the couple with the 0.51 mm Au element. The minimum differences found at the deepest immersions most likely reflect the closest approach to thermal equilibration of the movable elements in the MJ-1 couples to the fixed point temperature, while the maximum differences include additional non-equilibrium differential errors. In any case none of these differences is larger than a few hundredths °C.

To conclude this section, Fig. 15 presents direct comparisons of the two SRJS thermocouples on plots scaled to emphasize the thermal conduction ramps and the variations in thermoelectric homogeneity. The terminations of the conduction ramps are sufficiently discrete that no uncertainty should exist in selecting adequate working immersions to eliminate any systematic stem immersion correction for the couples. The range of thermoelectric inhomogeneities displayed in this figure amounts to < 20 mK. The inhomogeneities are intrinsic to the particular thermoelements used; more homogeneous thermoelements result in an even better thermocouple (e.g. S[Pt12: Au35], Figs. 17-19).

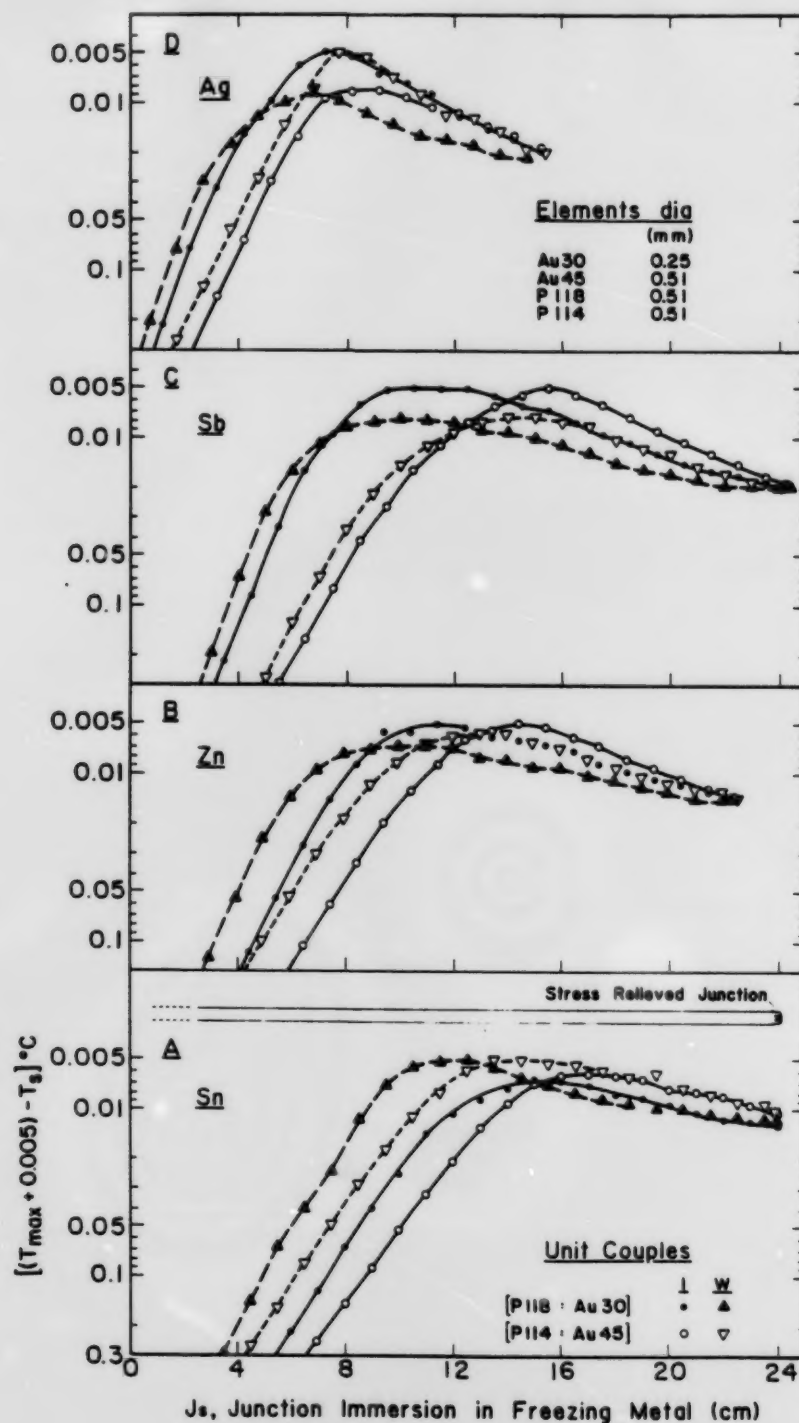


Fig. 15 Effect of Au wire diameter on the entrance immersion gradients of Pt/Au thermocouples in the Sn, Zn, Sb and Ag points.

Pt/Au and Pt/Pt10Rh (ASTM Type S) THERMOCOUPLES COMPARED AT FIXED POINTS

The foregoing account has clearly established that the Pt/Au thermocouple is a temperature sensor capable of exceptionally high performance in the range (0-1000)°C. The immersion-TEMF profiles of the Pt/Au and standard Pt/Pt10Rh couples at fixed points ranging from In to Ag are compared to illustrate the superior thermoelectric homogeneity attainable with the Pt/Au couple. The intrinsically degrading thermoelectric inhomogeneity that arises on exposing Pt10Rh elements in air to temperatures between ~ 150°C to 900°C is unavoidable. This inhomogeneity takes the form of a small enhancement in thermopower that is both temperature and time dependent on exposing the element to temperatures in the range (150-450)°C, while a larger degradation in thermopower, also temperature and time dependent, develops on exposing the elements in air to Rh oxidizing temperatures in the range (500-900)°C. The low temperature enhancement (LTE) bears similarities to the changes in thermopower associated with short range ordering and/or spinodal decomposition in alloys and the medium high temperature oxidation (MHTO) degradation appears related to the surface and internal oxygen content of the alloy. These two effects can alter the Seebeck TEMFs by the equivalent of $\lesssim 0.1$ K and $\lesssim 0.4$ K, respectively, in temperature determinations in the range to 1000°C [2-7]. Such effects vitiate any possibility of attaining the high degree of thermoelectric homogeneity in Pt10Rh elements that is necessary for both accurate and idealized thermocouple thermometry.

Figures 16 and 17, present immersion-TEMF profiles of typical Type S and Pt/Au couples, respectively, in fixed points operated at temperatures up to 420°C. At immersions greater than the thermal conduction-loss thresholds in the In (Figs. 16A, 17A) and Sn (Figs. 16B, 17B) points, the I and W profiles coincide within a few mK for both thermocouples. At these deep immersions, however, the profiles indicate inhomogeneity along the elements of the Type S couple equivalent in temperature to $\leq 10, 17$ mK and along the elements of the Pt/Au couple to $\leq 2, 4$ mK at In and Sn respectively.

At the Zn point the IWIW profiles (Fig. 16C) with the Type S couple reveal significant thermoelectric change due to the LTE thermopower effect on its Pt10Rh element during the ~ 4 h probings. At shallow ($J_s = 8$ cm) immersions, where the TEMF is generated in the furnace gradient along a segment of the Pt10Rh element that has been exposed deep in the fixed point to the thermopower enhancing temperature range (i.e. $\sim (150-420)^\circ\text{C}$) for the longest time, an increase in equivalent temperature of ~ 36 mK is seen between the I_1 and W_2 profiles. Figure 16C also shows a thermoelectric inhomogeneity equivalent to ~ 40 mK along the I_1 profile which is screened out on succeeding profiles as the thermopower of the alloy element is inhomogeneously enhanced by the in situ heat treatment during the measurements.

In contrast, the inhomogeneity unveiled on the corresponding immersion profiles of the Pt/Au couple at the Zn point, Fig. 17C, amount to the equivalent of ≤ 7 mK and multiple probing with this and

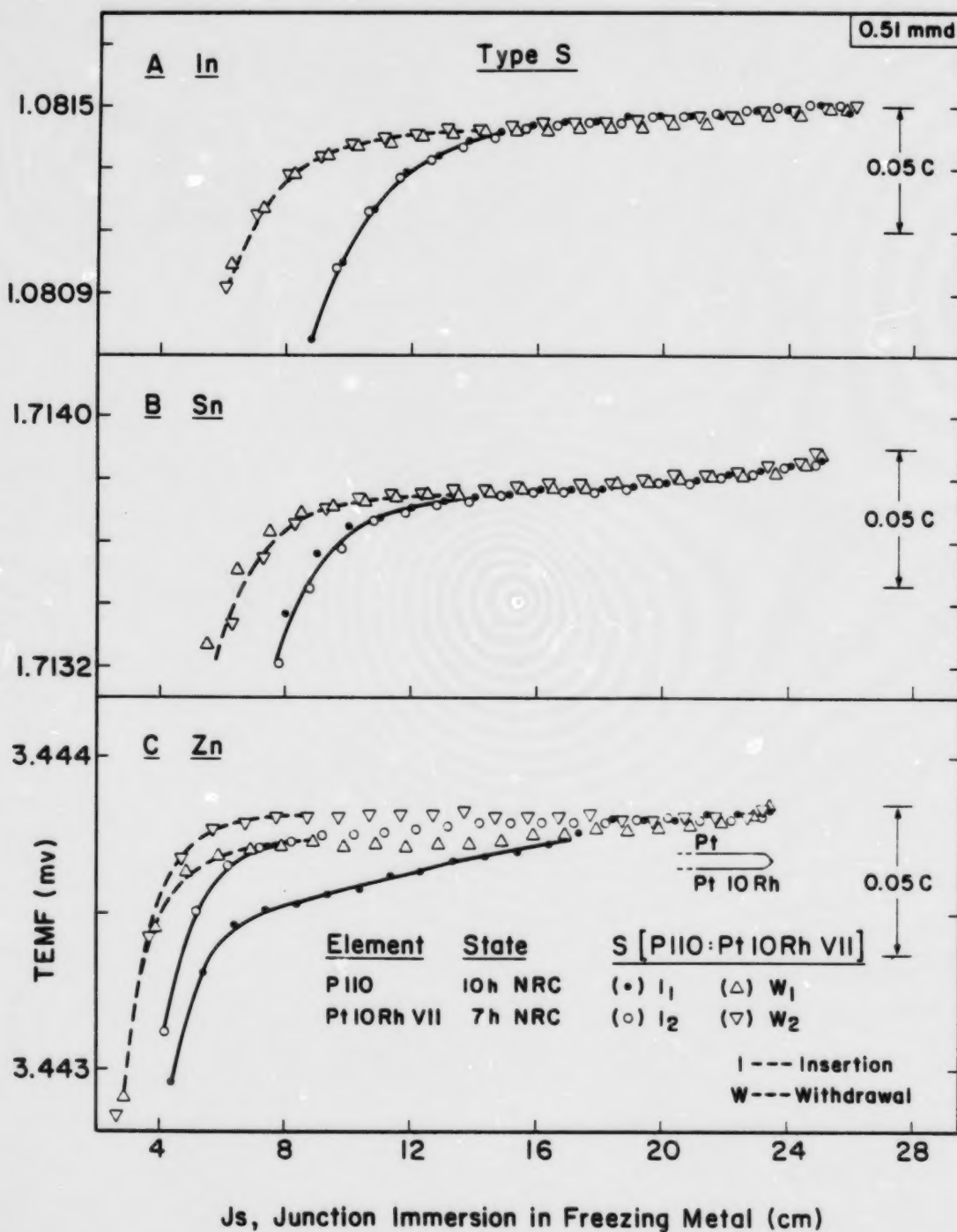


Fig. 16 Typical immersion profiles of a Pt/Pt10Rh thermocouple in the In, Sn and Zn points.

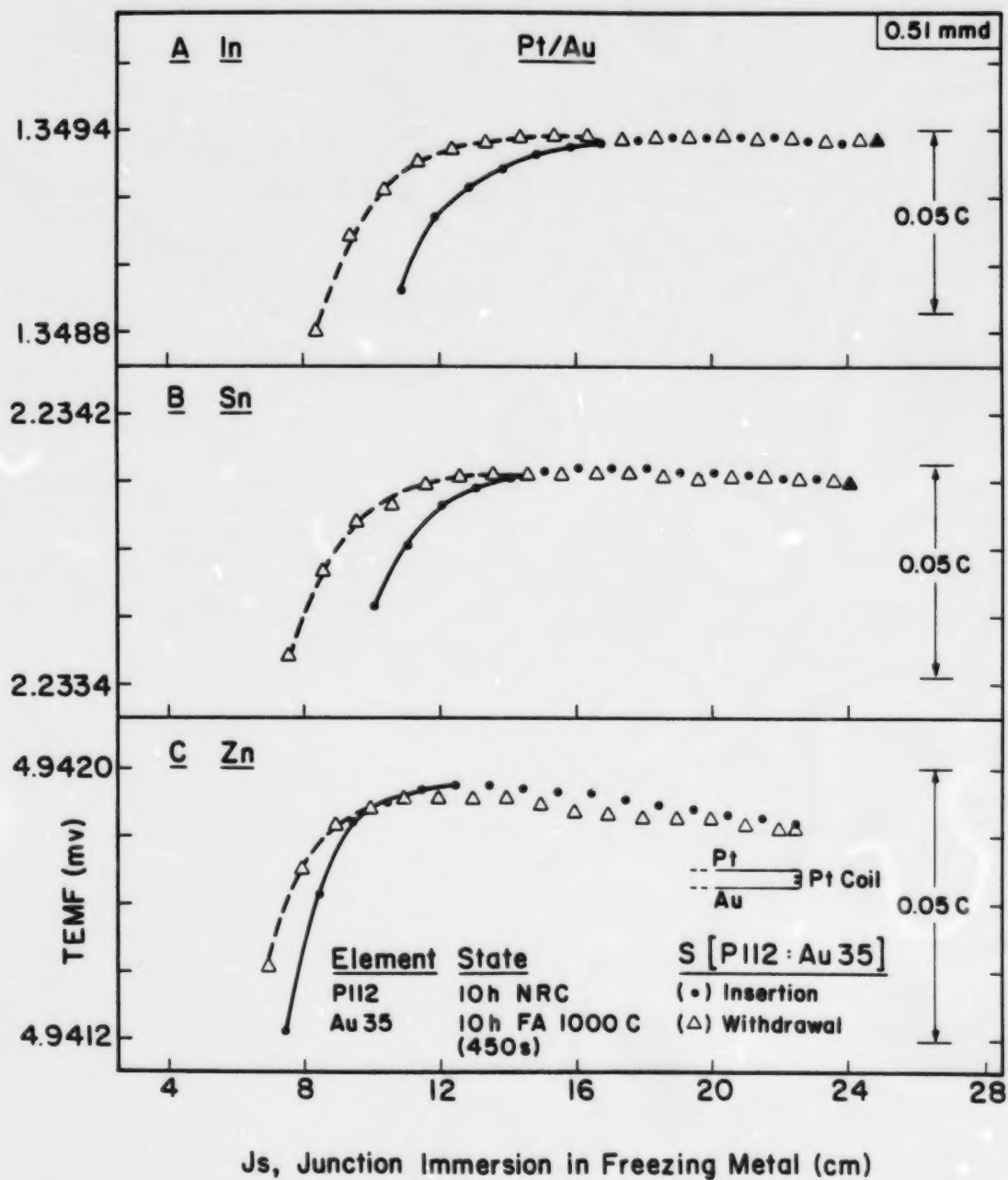


Fig. 17 Typical immersion profiles of a Pt/Au thermocouple in the In, Sn and Zn points.

other Pt/Au couples, stabilized with preparatory high temperature anneals, have shown no measurable thermoelectric changes that could be attributed to low temperature annealing effects in the Au or Pt elements.

At higher temperatures much larger thermoelectrically degrading changes occur on the Type S couples, as illustrated at the Sb (Fig. 18A) and Ag (Fig. 19A) points. Now, portions of the Pt10Rh elements are exposed in air to temperatures in the rhodium oxidizing range (500-900)°C. At immersions greater than the conduction thresholds, the first insertions of the couple, following fresh NRC preparatory annealing, track out immersion profiles at the Sb and Ag points that reveal rather small inhomogeneities, equivalent to ~ 0.01 K and 0.03 K respectively. In sharp contrast however, although the W_1 , I_2 , W_2 profiles nearly coincide, their corresponding inhomogeneities from conduction threshold to maximum immersion are dramatically increased to ~ 0.3 K in both fixed points. The degrading inhomogeneity arises simply from exposing the original oxide-clean alloy element to the furnace temperature gradient. The I_1 profile traces out a nearly flat immersion characteristic because during successive increments of insertion, the TEMF is generated, at each new step, along portions of the alloy element which, to that time, have had a common heat-treating history and hence a common inhomogeneity (partly oxide free, partly oxidized). The W_1 and the succeeding I_2 , W_2 profiles, on the other hand, are all characteristic of the alloy element in the inhomogeneously oxidized state attained at maximum immersion.

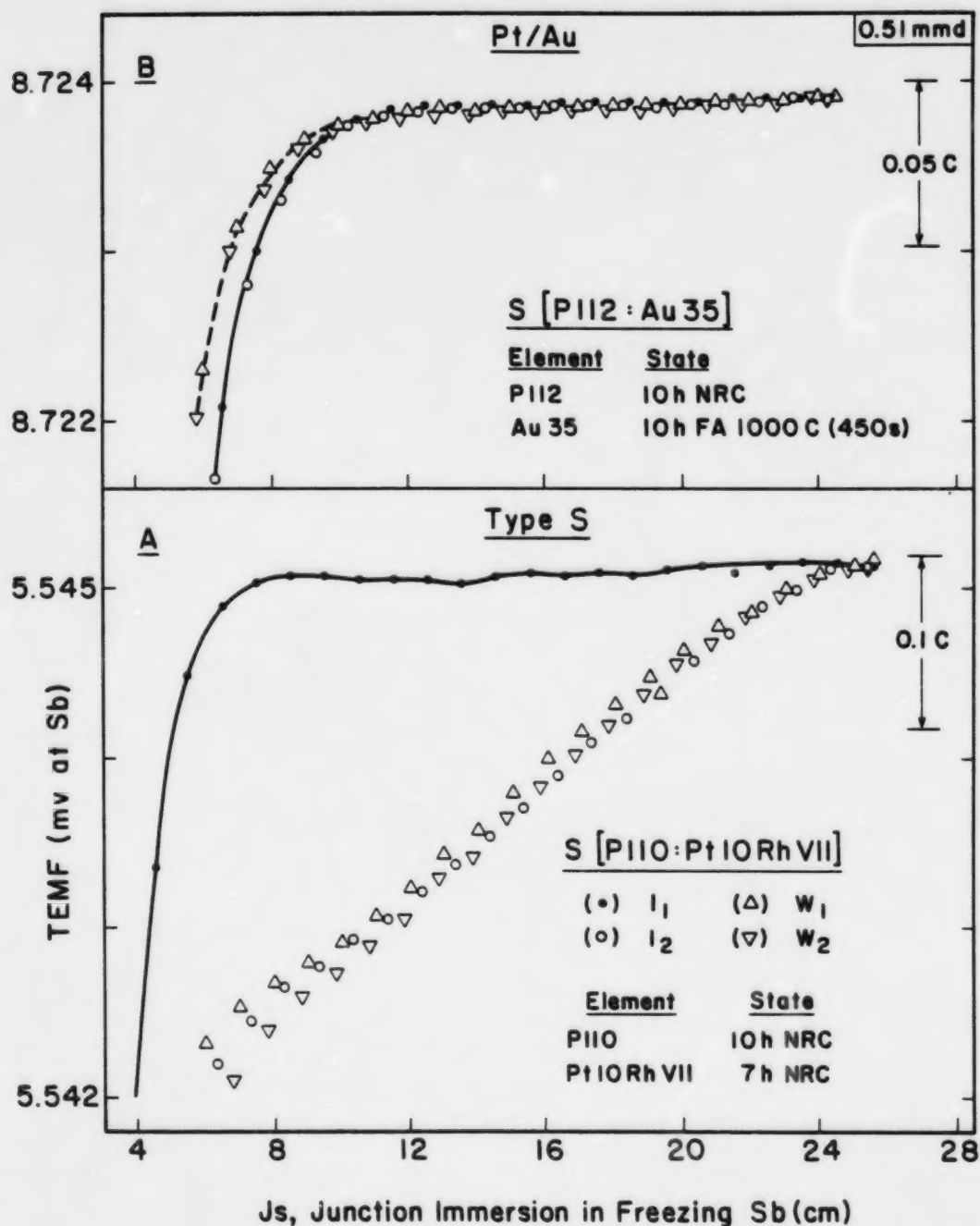


Fig. 18 Typical immersion profiles of a Pt/Pt10Rh couple, A, and a Pt/Au couple, B, in the Sb point.

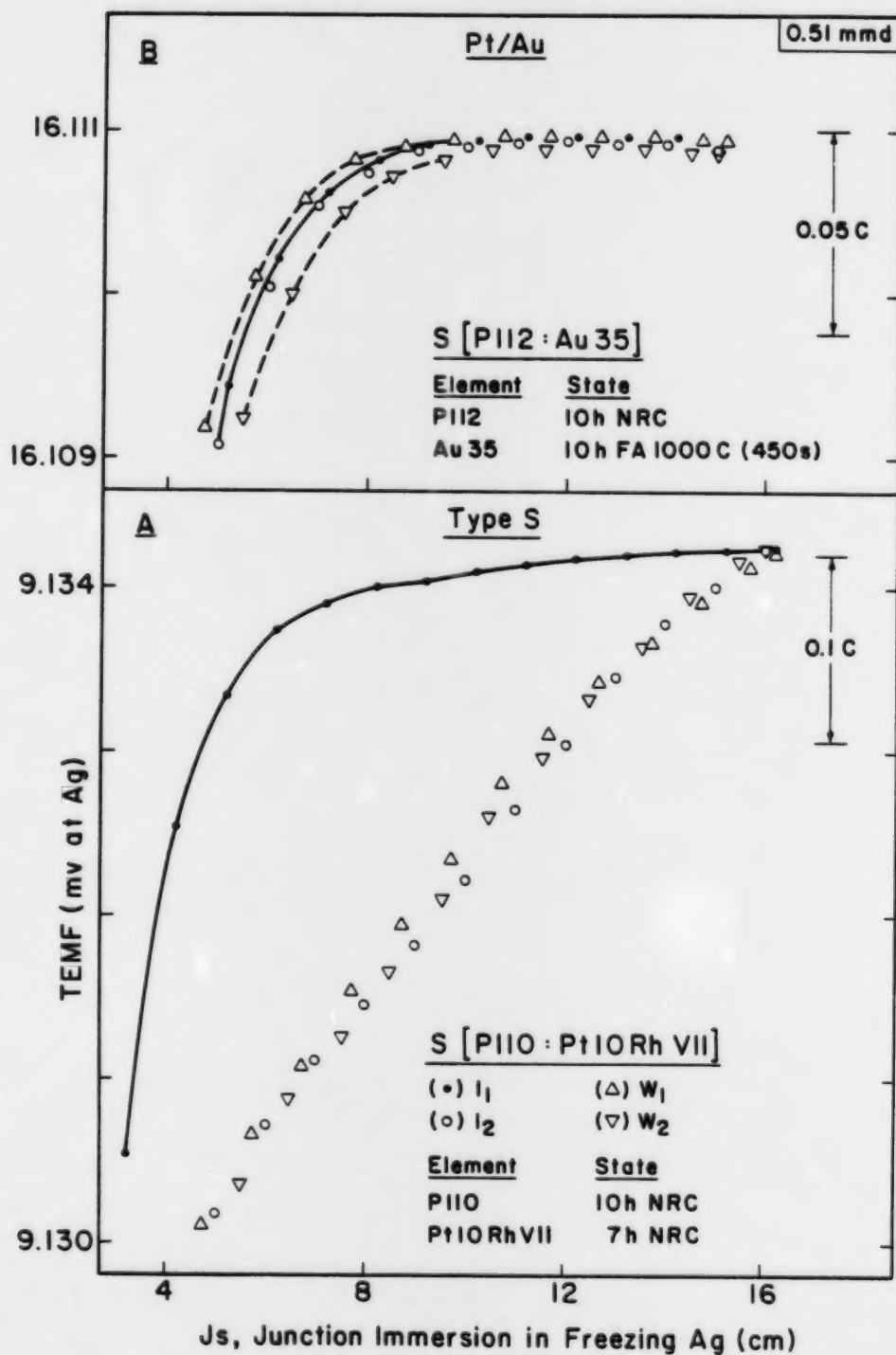


Fig. 19 Typical immersion profiles of a Pt/Pt10Rh couple, A, and a Pt/Au couple, B, in the Ag point.

Phenomenologically, the "oxygen-related degradation" in thermopower in the alloy element appears [4] in two stages, an initial instantaneous component followed by a slower degradation as the oxide layer thickens. The initial component gives rise to the nearly equivalent oxidation histories of the segment of the alloy element exposed at maximum immersion and results in the close agreement among the W_1 , I_2 , W_2 profiles in Figs. 18A, 19A.

At the Sb and Ag points the IWIW profiles determined on the Pt/Au couple, Figs. 18B, 19B, nearly coincide and from thermal conduction threshold to maximum immersion indicate thermoelectric inhomogeneities along the elements equivalent in temperature to $\lesssim 6$ mK — less than 1/50 the corresponding inhomogeneities on the Type S couple in Figs. 18A, 19A.

Following careful disciplined preparatory anneals on the elements of both couples to stabilize their thermopowers for sustained exposure to high temperature, Figs. 16-19 clearly illustrate that the Pt/Au couple has distinct advantages over the standard Pt/Pt10Rh thermocouple for temperature measurements up to 1000°C. The immersion-TEMFs of the couples in the isothermal fixed points show that, overall, the degree of thermoelectric homogeneity attained along the elements of the Pt/Au couple is strikingly superior to that manifested by the elements of the Type S couple. Substituting a Au element for the alloy element in the standard couple eliminates the thermoelectrically degrading effects of LTE and MHTO on the thermopower of the Pt10Rh elements. Whereas the Type S couple, at immersions

greater than the thermal conduction-loss thresholds in the Sb and Ag points (Fig. 18A, 19A), is clearly immersion-dependent to the order of ~ 0.3 K, the Pt/Au couple (Fig. 18B, 19B) in the same fixed points is thermoelectrically homogeneous to better than 0.01 K. Both Au and Pt thermoelements may be heat-treated and maintained in states of high thermoelectric homogeneity for service to 1000°C. In contrast, a Pt10Rh thermoelement may be prepared and maintained in a state of good homogeneity for exposures at low temperatures (e.g. Fig. 16A, 16B and [4]) but the thermoelectrically degrading effects of LTE and MHTO at higher temperatures cannot be avoided. It is these properties of the alloy element that are the root causes of the inferior performance of the Type S couple as a precise temperature sensor.

The Pt/Au couple has two minor disadvantages in comparison with the Type S couple. First, an upper operating temperature limit of 1000°C is recommended to avoid any grain boundary melting and lead separation in the Au element. This limit will not seriously restrict the usefulness of the Pt/Au couple, even as a scaling instrument, because there are already strong indications [8-16] that the upper limit of the high temperature platinum resistance thermometer (HTPRT) will be set at the Ag point for reasons of ensuring adequate electrical insulation, chemical stability, grain growth control and mechanical integrity in the platinum resistor and its four platinum leads. Secondly, for elements of the same diameter, the thermal conduction thresholds of Pt/Au couples, due to the higher thermal conductivity of Au elements, are 2-3 cm greater in our experimental arrangements than

for Type S couples. For a sensor capable of working to precisions of 10 or 20 mK at high temperatures, an extra 2-3 cm immersion is not a significant limitation to ensure thermal equilibration of the couple; if necessary, the element diameter could be halved which would reduce both the necessary threshold immersion (Table I) and the mass (and hence cost) of gold in the couple.

These critical comparisons at the metal fixed points show that the Pt/Au thermocouple clearly outperforms the standard Pt/Pt10Rh (Type S) thermocouple as a precise thermoelectric temperature sensor in the range (0-1000)°C.

Indeed, the Pt/Au couple should also be considered as a suitable and challenging alternative to the HTPRT for many practical but precise temperature measurements in this range. The HTPRT has now been developed to the stage where temperature measurements at the Ag point on a resistance wire scale are repeatable to a few mK [9-11, 15, 26] and accurate to about 10 mK. The HTPRT, however, is expensive [5 K (US\$)] and fragile [12] and requires either a dc resistance comparator bridge [30 K (US\$)] or an ac resistance comparator [25 K (US\$)] to meter [30-33] electrical resistance. In contrast, a normal SRJS Pt/Au thermocouple with 186 cm long, 0.5 mm diameter thermoelements has a material value of ~ 600 (US\$) and requires only a superior DVM (e.g. Keithley 181, ~ 4 K (US\$)) to meter the potentiometric measurements. This study has shown that the Pt/Au thermocouple, following suitable high temperature preparatory annealing, is also capable, of repeatabilities of a few mK at the Ag point and the uncertainties in

temperature measurements arising from the intrinsic thermoelectric inhomogeneities along the Pt and Au elements can be reduced to 10 or 20 mK. Even with doubling these intrinsic uncertainties to account for differences between working environments as opposed to calibration experimental arrangements, it is reasonable to expect that routine uncertainties in temperature measurements on a Pt/Au thermoelectric wire scale near 1000°C would be < 50 mK. Reducing the measurement temperature, in common with platinum resistance thermometry, improves the accuracy attainable in the thermoelectric thermometry. Further, on the basis of cost, simplicity of construction, ruggedness, and even salvageability of damaged thermoelements by reanneal and reassembly procedures, the Pt/Au couple has distinct advantages over the more sophisticated HTPRT for many temperature measurements.

CONCLUSION

The outstanding performance of the Pt/Au thermocouple as a thermoelectric temperature sensor fully justifies that it should be given serious consideration as a superior replacement for the standard Pt/Pt10Rh (Type S) thermocouple in the temperature range (0-1000)°C and as a worthy alternative to the high temperature platinum resistance thermometer in the range (500-1000)°C.

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THE Pt/Au THERMOCOUPLE: II. PREPARATORY HEAT TREATMENT,
WIRE COMPARISONS AND PROVISIONAL SCALE

E.H. McLAREN and E.G. MURDOCK

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WIRE COMPARISONS AND PROVISIONAL SCALE

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THE Pt/Au THERMOCOUPLE: II. PREPARATORY HEAT TREATMENT,
WIRE COMPARISONS AND PROVISIONAL SCALE

E.H. McLaren and E.G. Murdock

ABSTRACT

Part II describes investigations on the effects of 450°C to 1000°C heat-treatments on the thermoelectric stability and homogeneity of high purity Au wire that led to the preferred preparatory anneal that understructures the superior performance of Pt/Au thermocouples described in Part I. Comparisons of the thermoelectric effects of up to 100 h heat-treatments at uniform temperatures up to 1000°C on many high purity Au wires from a single refined batch, from batch-to-batch from a single refiner, and from batches produced by two refiners are presented. Extensive thermoelectric intercomparisons at six temperatures (160, 232, 420, 639, 786, 967)°C of Au elements from 7 batches and Pt elements from 9 batches following recommended NRC preparatory anneals are presented to give an overview of the variations that may be expected in selecting wire for Pt/Au thermocouples. A provisional Pt/Au thermocouple table deduced from fitting a 5th degree polynomial to calibration data from a single thermocouple at the In, Sn, Zn, Sb, AgCu and Ag points is given.

INTRODUCTION

Part I of this paper [1] described the basic properties of the Pt/Au thermocouple when the thermoelements are prepared with the NRC-preferred preparatory anneals, assembled in regular twin-bore alumina sheaths and lead harnesses, and, in addition, the junction joining the thermoelements incorporates a small stress-relieving coil to remove the thermoelectric effects of stress arising from the differential thermal expansions of the elements. Part II surveys the studies of the thermoelectric effects of heat-treating Au wire which resulted in the selection of the NRC-preferred preparatory anneal for Au elements; similar studies on Pt elements having been adequately documented elsewhere [2, 3]. Part II also includes intercomparisons of Au and of Pt wires from several batches, supplied by two refiners of each element, to determine the thermoelectric variations to be expected from suitably heat-treated and stabilized wire selected for thermoelectric thermometry in the range 0°C to 1000°C. Such knowledge is relevant in considerations involving a thermoelectric wire scale, the method of calibration, and the applicability of the Pt/Au thermocouple.

A. APPARATUS AND PROCEDURES

a) FORM OF COUPLES

With the exception of the data shown in Figs. 1A, B, (obtained before the significance of the thermoelectric effects of stress arising from differential thermal expansions of Au and Pt elements was fully appreciated), the Pt/Au couples used in Part II were fabricated in the SRJS (stress relieved junction sheathed couple) mode incorporating the stress-relieving coil as described in Part I. The Au and Pt wire comparisons were carried out in separate, regular-junction, comparison thermocouples of Au/Au or Pt/Pt respectively, using normal twin-bore alumina thermocouple sheaths and lead harnesses. Au wires were compared with a new Au reference element (Au45:JM84) and Pt wires with a new Pt reference element (Pt(P114):E85). These reference wires initially received their respective Au and Pt NRC preparatory anneals and the alumina sheaths were prebaked for 44h at 1000°C.

b) WIRE IDENTIFICATION

This study investigated Au wires with nominal purities of 99.999(59) and 99.99(49) wt% refined by Johnson Matthey Ltd. (JM) and Sigmund Cohn Corp. (SC), and thermometric reference grade (R, nominally 59 grade purity) Pt wires refined by Engelhard Industries (E) and Sigmund Cohn Corp. (SC). Separately refined batches of wire are identified using the source initials and the year of purchase; e.g. Au45:JM84 identifies Au element 45 from a roll of Au wire refined by Johnson Matthey Ltd. and purchased in 1984. In all cases wire from different orders from the same refiner were drawn from different

ingots. Table I summarizes the sources, grades, and diameters of the thermoelements that were examined.

c) PREPARATORY HEAT TREATMENT

Preparatory heat treatments are necessary to stabilize the thermopowers of thermoelements for use in desired temperature ranges. Heat treatment removes and stabilizes physical defects, introduced by cold-working deformations during manufacture and subsequent manipulations of the wire, by the processes of normal stress relieving and recrystallization annealing. High temperature annealing for longer periods, than those needed for strain annealing, effects a measurable thermal refinement in the elements by removing, altering, or dissociating some oxidized impurity solutes by diffusion and evaporation, oxidation or deoxidation processes which usually firmly stabilize the chemical impurity contents in the elements for sustained service at lower temperatures.

i) Platinum: The NRC-preferred preparatory anneal on new Pt wire is a two-stage electric wire anneal (WA) on the full thermoelement length, 10 h at 1300°C followed by a 1 h vacancy anneal at 450°C; in turn followed by a terminating overnight vacancy anneal on the sheathed length of the assembled couple [2, 3].

ii) Gold: Initially, conventional [4] AC electric wire anneals disclosed two major disadvantages at the highest annealing temperatures: the masses of both the full length (186 cm) and the shorter (62 cm) hot junction segments, hanging either as straight elements or as looped catenaries, were sufficient to cause stretching

TABLE I: THERMOELEMENTS

<u>Source</u>	<u>Grade</u>	<u>Diam</u> (mm)	<u>Elements</u>
			<u>Au</u>
SC82	59	0.51	6, 8, 14, 16, 18, 20, 22, 24
SC84	59	0.51	26, 28
SC85	59	0.25	30
JM80	49	0.51	49
JM82	59	0.51	7, 9, 15, 19, 21, 23, 25, 27
JM84	59	0.51	31, 33, 35, 45, 47
JM85	49	0.25	41, 43
			<u>Pt</u>
SC65	R	0.51	P121
SC70	R	0.51	SC7, P118, P120
SC70	R	0.25	P122
SC86	R	0.51	P123, P124
E72	R	0.51	P3, P21, P119
E73	R	0.51	P35
E81	R	0.51	P103, P104, P116, P117
E83	R	0.51	P108, P109, P110, P111, P112
E85	R	0.51	P114

SC Sigmund Cohn Corp.
 JM Johnson Matthey Ltd.
 E Engelhard Industries

and even separation of the elements, most frequently at points of maximum stress near the power terminals; in addition, due to the high thermal conductivity of Au, substantial temperature inhomogeneity was evident along the annealing elements — several cm of the elements from the power terminal to the threshold for thermal conduction loss could not attain the desired annealing temperature. The conduction-loss length can be reduced by the use of conduction restrictors, but, even then, to attain a reasonable ($\pm 10^\circ\text{C}$) homogeneity in temperature along the annealing element, it was necessary to enclose the straight (62 cm) element in a vertical cylindrical silica tube (10 cm id), control convection losses in the gas surround using a metered air purge to the heating chamber, and employ a bottom coil in the electrical feed connector to compensate for thermal expansion of the Au element during heating. As a consequence of these complications, we have found that the preparatory heat treatments on Au elements are both simpler and more reliable when furnace anneals (FA) are used.

The furnace anneal (FA) uses a 71cm three-winding vertical Inconel block furnace capable of being balanced to $\pm 1^\circ\text{C}$ over a length of 62 cm at temperatures up to 1000°C . The block has six heat-treating wells lined with silica tubes (10/8 mmd). Segments of Au elements (62 cm), are placed in turn, into the wells in separate silica tubes (7/5 mmd) open to air for heat treatment. These heat-treated segments of the Au elements exceed the length (47 cm) of the hot

junction segments of the thermocouples that are exposed to the temperature gradient in NRC fixed-point furnace arrangements. Three 62 cm segments of heat-treated Au wire are rewelded to form one (186 cm) Au thermoelement.

For this investigation Au wires were furnace annealed for various durations at (800, 900 and 1000)°C; also included are results of an earlier series of experiments using electric wire annealing in air at 740°C. Following the high temperature annealing the Au elements were assembled into regular thermocouple sheaths and lead harnesses and paired and welded to either a Pt or a Au reference element as thermocouples for measurement. The reference elements received the preparatory anneals for Pt and Au (summarized later Section B (f)) wire. Routinely, Pt/Au couples received overnight sheathed anneals at 450°C (450s), and unless otherwise indicated, Au/Au couples > 2 h sheathed anneals at 450°C. The 450°C anneal serves both as a good vacancy defect anneal for Pt elements, and as a general recovery anneal for Au elements that are either deformed by cold-working or contain excess defect concentrations arising from high temperature quenching.

B. HEAT TREATMENT OF AU WIRE

a) OVERALL EFFECT OF THE TEMPERATURE AND DURATION OF THE PREPARATORY ANNEAL

The study begins with an examination of the effects of separately heat-treating the Au elements on the Seebeck TEMFs generated in Pt/Au thermocouples at the Sb point. The long Sb ingot provides >15

cm immersion length, in addition to the minimum immersion required to avoid lead thermal conduction losses, to examine thermoelectric inhomogeneity along thermoelements — 28 cm long Ag melts have not yet been established in this laboratory. Figures 1 and 2 show insertion-withdrawal (IW) immersion-TEMF profiles for Pt/Au couples having Au thermoelements in as-received (AR, refiner's final anneal) states and in various heat-treated states. Table II summarizes the corresponding TEMFs that were measured at maximum immersion in the freezing Sb.

The immersion characteristics, Figs. 1A, B, after electric WA at 740°C were measured with couples having regular welded junctions and therefore reveal the hysteretic IW loops associated with differential thermoelement expansions as discussed in Part I [1]; for the furnace annealed series all Pt/Au couples incorporated the stress-relief coil in their junctions. The changes, following heat treatment, in the magnitude of the TEMF at the Sb point from values determined in the AR state, reflect changes in the thermopower of Au elements arising from thermally-activated internal stress-relief and stabilization of chemical impurities at the particular annealing temperature. As emphasized in Part I, both the magnitude and the variation (i.e. thermoelectric inhomogeneity) of the Seebeck TEMF on insertion-withdrawals of a thermocouple in fixed points provide basic information on the quality of the thermocouple for precise thermometry.

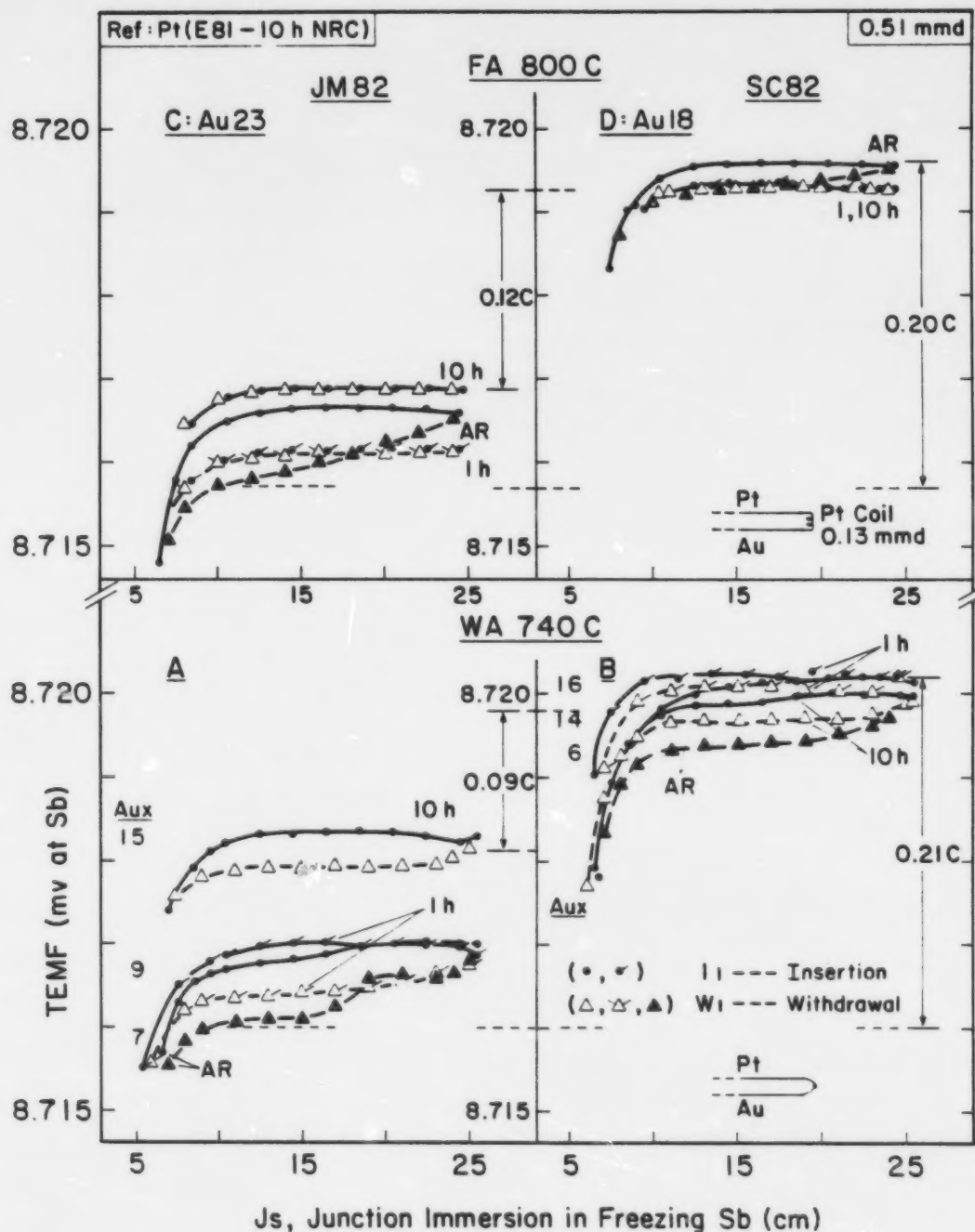


Fig. 1 Thermoelectric effects at the Sb point of heat-treating Au thermoelements from two sources on the immersion-TEMP characteristics of couples referenced to Pt: A, B and C, D respectively, after electric wire anneals (WA) at 740°C and after furnace anneals (FA) at 800°C; included are measurements on as-received (AR) wire.

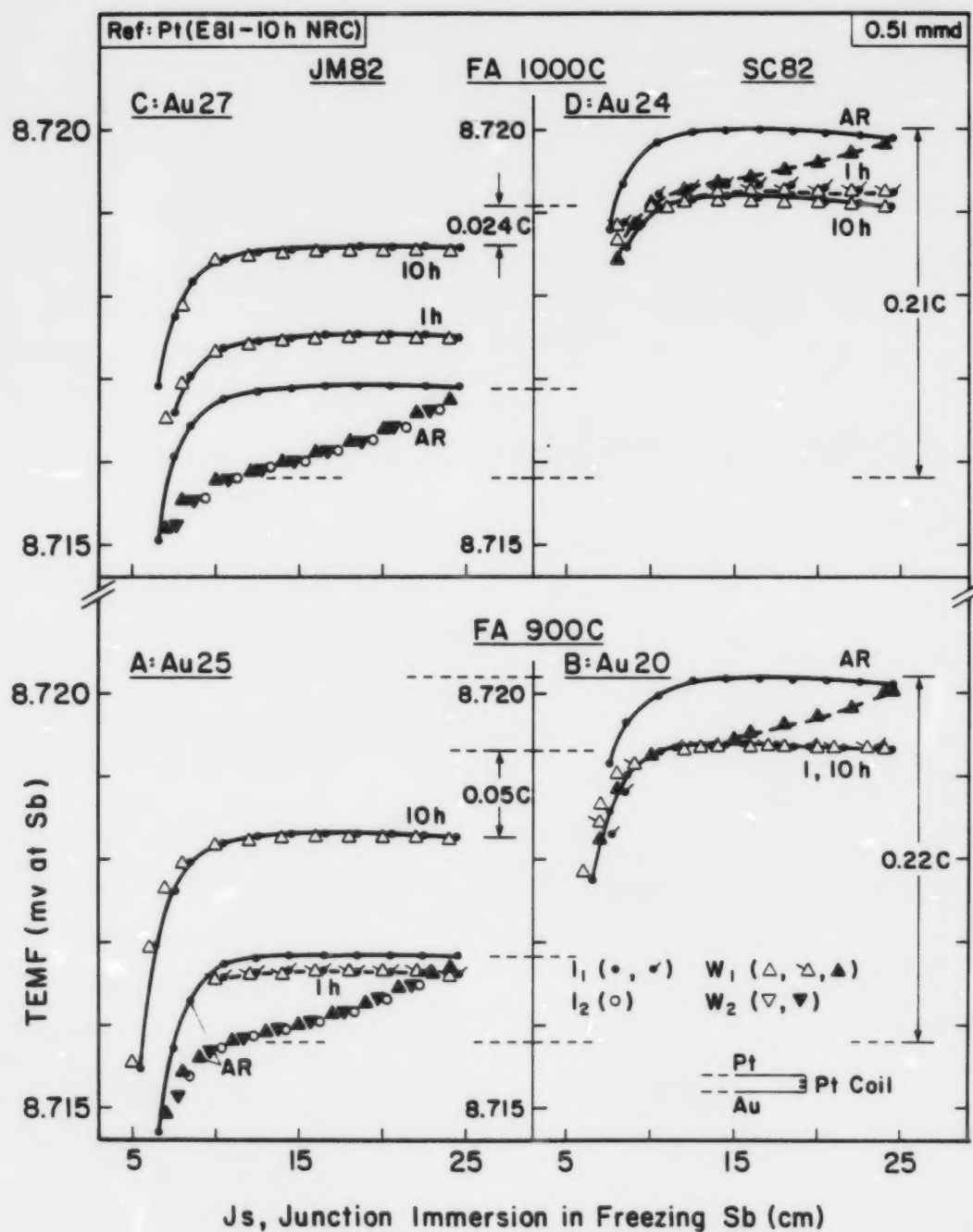


Fig. 2 Thermoelectric effects at the Sb point of heat-treating Au thermoelements from two sources: A, B and C, D respectively, after FA anneals at 900°C and 1000°C.

TABLE II: Thermoelectric Comparison of Heat-treated Au Wires from Refined Batches, JM82 and SC82

State	JM82 [ref. Pt(P104)]				SC82 [ref. Pt(P103)]			
	Element	TEMF mv at Sb ^a	10 h-AR μ v	Element	TEMF mv at Sb ^a	10 h-AR μ v	μ v	°C
AR 1 h WA740 10 h WA740	7	8.7168		6	8.7198		3.0	0.15
	9	7168		16	7202		3.4	0.17
	15	7182	+ 1.4	14	7199	+ 0.1	1.7	0.09
AR 1 h FA800 10 h FA800	23	8.7166		18	8.7195		2.9	0.15
	23	7162		18	7193		3.1	0.16
	23	7169	+ 0.3	18	7193	- 0.2	2.4	0.12
AR 1 h FA900 10 h FA900	25	8.7168		20	8.7201		3.3	0.16
	25	7166		20	7193			0.14
	25	7183	+ 1.5	20	7193	- 0.8	1.0	0.05
AR 1 h FA1000 10 h FA1000	27	8.7169		24	8.7199		3.0	0.15
	27	7175		24	7192		1.7	0.09
	27	7186	+ 1.7	24	7191	- 0.8	0.5	0.02

(a) maximum immersion

Overall considerations of the effects of heat-treating the Au elements revealed in Figs. 1, 2 and in Table II lead to the following observations: (1) Au wire in AR state from both refiners is thermometrically unstable to heat treatment in the gradient of the Sb furnace — W_1 profiles depart as much as 0.05°C from the I_1 profile; (2) uniform annealing at temperatures $> 800^\circ\text{C}$ results in thermoelectrically homogeneous wire but the thermopowers of JM82 elements and to a much lesser extent SC82 elements are dependent on the duration of the anneal; (3) the flat IW profiles at the Sb point shown for these Pt/Au couples with Au elements prepared with 10 h FA anneals at 800°C , 900°C , and 1000°C imply, along the 15 cm length exceeding the thermal conduction-loss thresholds, a combined thermoelectric homogeneity in the Au and Pt elements of $< 0.2 \mu\text{V}$ (equiv. 0.01°C); (4) at maximum immersion the TEMF differences between JM82 and SC82 wires were the equivalent of $\sim 0.17^\circ\text{C}$ in AR state but only $\sim 0.05^\circ\text{C}$ and $\sim 0.024^\circ\text{C}$ following 10 h FA anneals at 900°C and 1000°C , respectively — clearly heat treatment effected some refinement in the wires, prominently in JM82 wire; (5) heat treatment increased (more positive) the thermopower of JM82 wire and decreased (more negative) the thermopower of SC82 wire — likely due to intrinsic differences and subsequent alterations in the content or state of the chemical impurities in the gold arising from both differences in the source (ore) and method of refinement; (6) the differences in TEMF with Pt/Au

couples using Au elements from the same source, annealed for 10 h at 900°C and 1000°C, are small ($< 0.2 \mu\text{v}$, equiv. to $\sim 0.01^\circ\text{C}$ at Sb).

b) RELATIVE THERMOELECTRIC INHOMOGENEITY ALONG HEAT-TREATED AU
WIRE

For part of this comprehensive intercomparison of the effects of heat-treating Au wires, a simpler and more practical, though somewhat less precise, method was used than that employed in the preceeding Section B(a). The metal freezing point furnaces were utilized as highly stable thermal comparators only, the melts being held molten a few degrees above their liquidus points. In most respects, for comparative thermoelectric measurements, the highly stabilized and well-balanced furnace blocks serve almost as well as secondary fixed points since the gradient zones in such furnaces are nearly indistinguishable from those existing in the same furnaces during authentic freezing or melting transformations.

For the comparisons, one Au element (Au45:JM84) was given a preferred stabilizing anneal (10 h FA at 1000°C) and was designated the reference element to which all other Au elements were compared when assembled as a Au/Au thermocouple. Element Au45 was selected primarily because it had already been used in prior work (Figs. 11, 13, 15 Part I, [1]) on the relationships between the thermoelectric properties of the Pt/Au thermocouple and its individual elements.

Since the test and the reference Au elements are both exposed to the standing throat gradient in the metal point furnaces, paired 0.51 mm elements should have nearly identical thermal conduction-loss

properties. The Seebeck TEMF generated in the Au/Au couple in these furnaces, therefore, should reflect primarily differences in thermopower arising from intrinsic impurity contents and thermoelectric inhomogeneities due to both batch and heat-treating differences in the two elements.

The test couples were inserted at maximum immersion (see Fig. 10 and Ref. [1]) into the all-liquid metal freezing point cells. Maximum insertion allows enough (~ 12 mm) clearance between the tip of the ceramic sheath and the bottom of the insert thermocouple well to accommodate both the thermocouple junction and the thermal expansion of the Au elements over the range 20°C to 1000°C . Following insertion and ~ 16 min thermal equilibration time, TEMFs were measured at maximum immersion and at three other immersions by withdrawing the couple in 5 cm increments, using 4 min thermal equilibration times. Such comparisons were made at (160, 235, 420, 639, 786, 967) $^{\circ}\text{C}$; temperatures remained steady to within a few mK over the 24 min period required to withdraw and then return the couple for remeasurement at maximum immersion, including the initial and final potentiometric zero and standard cell normalizations.

These comparisons of particular Au thermoelements with reference Au45 at each temperature yield both a Seebeck TEMF relative to Au45 at each test immersion and also the variation in thermoelectric inhomogeneity along the elements as previously immersed 15 cm lengths are removed from the gradient zones of the furnaces.

After fabrication each Au(x)/Au45 couple received an initial overnight sheathed FA at 450°C (450s) as a general stress-relieving anneal. Figure 3 shows how the relative inhomogeneities of two Au wires from refined batches JM84 and SC84, measured in all-liquid Sb and Ag freezing point cells at 639°C and 967°C, altered following successive furnace anneals with increasing duration at 900°C and 1000°C. The very small differences with immersion in the relative Seebeck TEMF from that measured at maximum immersion emphasize the high degree of thermoelectric homogeneity that exists in most heat-treated 59 grade Au elements.

General comments on the effects of heat treatments varying from 1 h FA at 900°C to 100 h FA at 1000°C on elements Au47 and Au28 are: (1) following uniform furnace anneals at 900°C and 1000°C, the maximum relative inhomogeneities observed on withdrawing the couples 15 cm from the Sb and Ag furnaces amounted to $< 0.3 \mu\text{v}$ at Sb and $< 0.4 \mu\text{v}$ at Ag, equivalent to $< 0.016^\circ\text{C}$ in temperature measurements with a Pt/Au couple at these temperatures; (2) following furnace anneals varying from 10 h to 100 h at 1000°C, relative inhomogeneities equivalent to $< 0.01^\circ\text{C}$ are shown in Figs. 3A, C for Au47; (3) the relative inhomogeneities in both elements appears to be highly stable to heat treatment at 1000°C; (4) 1 h FA at 900°C would be an inadequate heat-treatment to prepare these elements for sustained exposure to 1000°C; (5) since the absolute inhomogeneity along the reference element Au45 is unknown (due to instrumental deficiencies in the

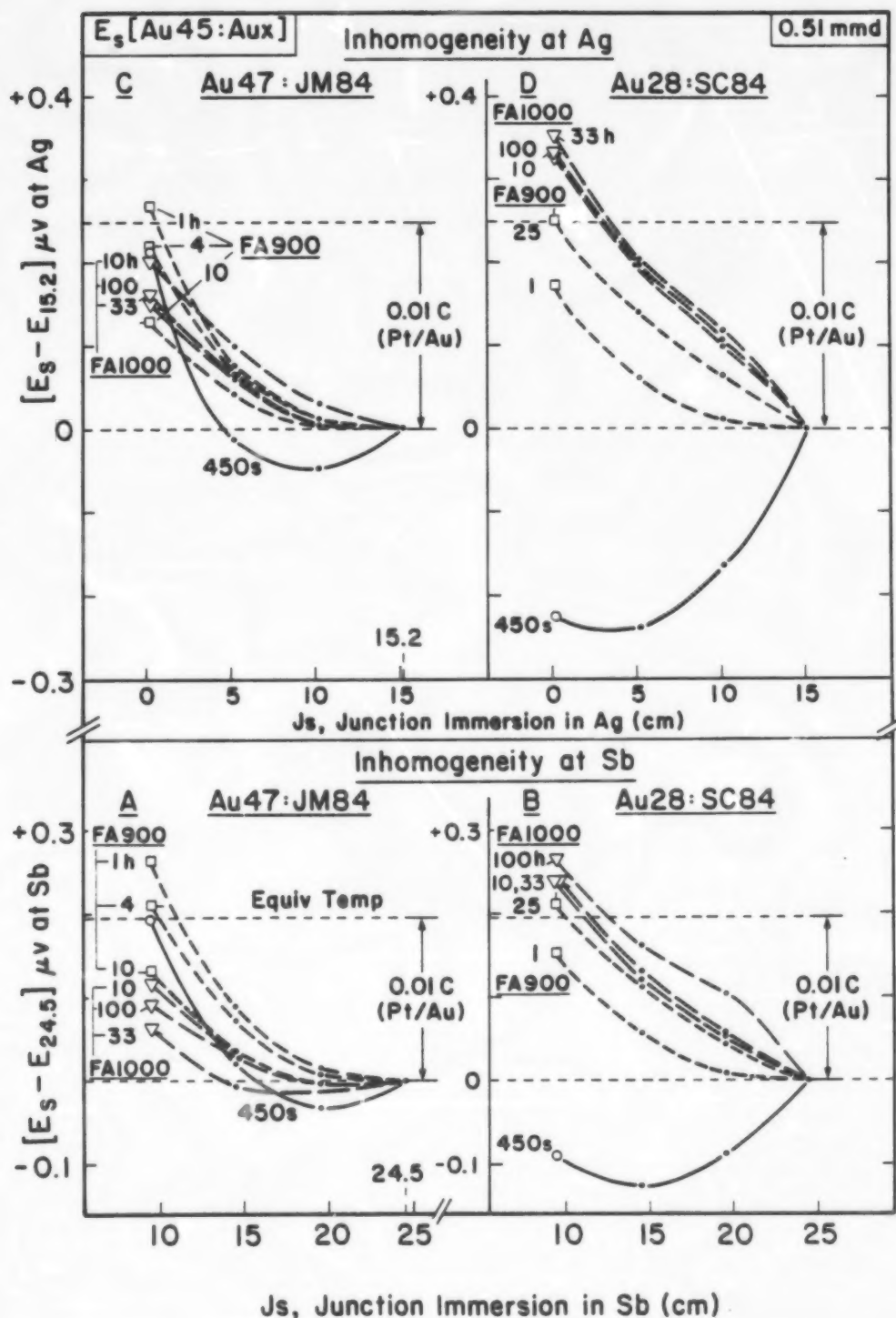


Fig. 3 Thermoelectric inhomogeneity along Au thermoelements from two sources relative to reference element Au45 at the Sb and Ag points following preparatory anneals at 450°C, 900°C and 1000°C.

type MJ-1 couple at these sensitivities and temperatures, discussed in [1]), the absolute thermoelectric inhomogeneities of elements Au47, Au28 would be either increased or decreased from the relative values shown in Fig. 3 by amounts embracing the inhomogeneity of the reference element; (6) the 450s stress-relief anneal for Au wire is, not surprisingly, entirely inadequate as a preparatory anneal to stabilize Au elements for precise measurement of high temperatures.

c) LONG DURATION HEAT TREATMENT AT 900°C AND 1000°C

The effects of long duration uniform anneals on the Seebeck TEMFs generated in the gradient of the stabilized Sb fixed point furnace at 639°C of 59 grade Au elements from several [JM82, 84; SC82, 84, 85] refined batches are presented in Figs. 4 and 5. Most of the data comprise TEMF measurements made following furnace anneals at 900°C and 1000°C but some pre-FA900°C measurements in AR, 450s and FA800°C anneal states are included and lumped as ordinates at 0 h on the duration axis. The figures include measurements at two immersions ($J_s = 24.5, 14.5$ cm) at each annealing step.

Figures 4 and 5 indicate that: (1) Au wires from batches JM82, 84 are thermoelectrically unstable (Fig. 4) to the FA900°C anneals, a characteristic of JM wire already revealed in the IW immersion-TEMF profiles, Fig. 2A, referenced to Pt, on heat-treating Au25:JM82 at 900°C; (2) Au wires from batches SC84, 85, however, are relatively stable (Fig. 5) to the FA900°C anneal, in agreement with the annealing performance at 900°C shown in Fig. 2B for Au20:SC82; — the

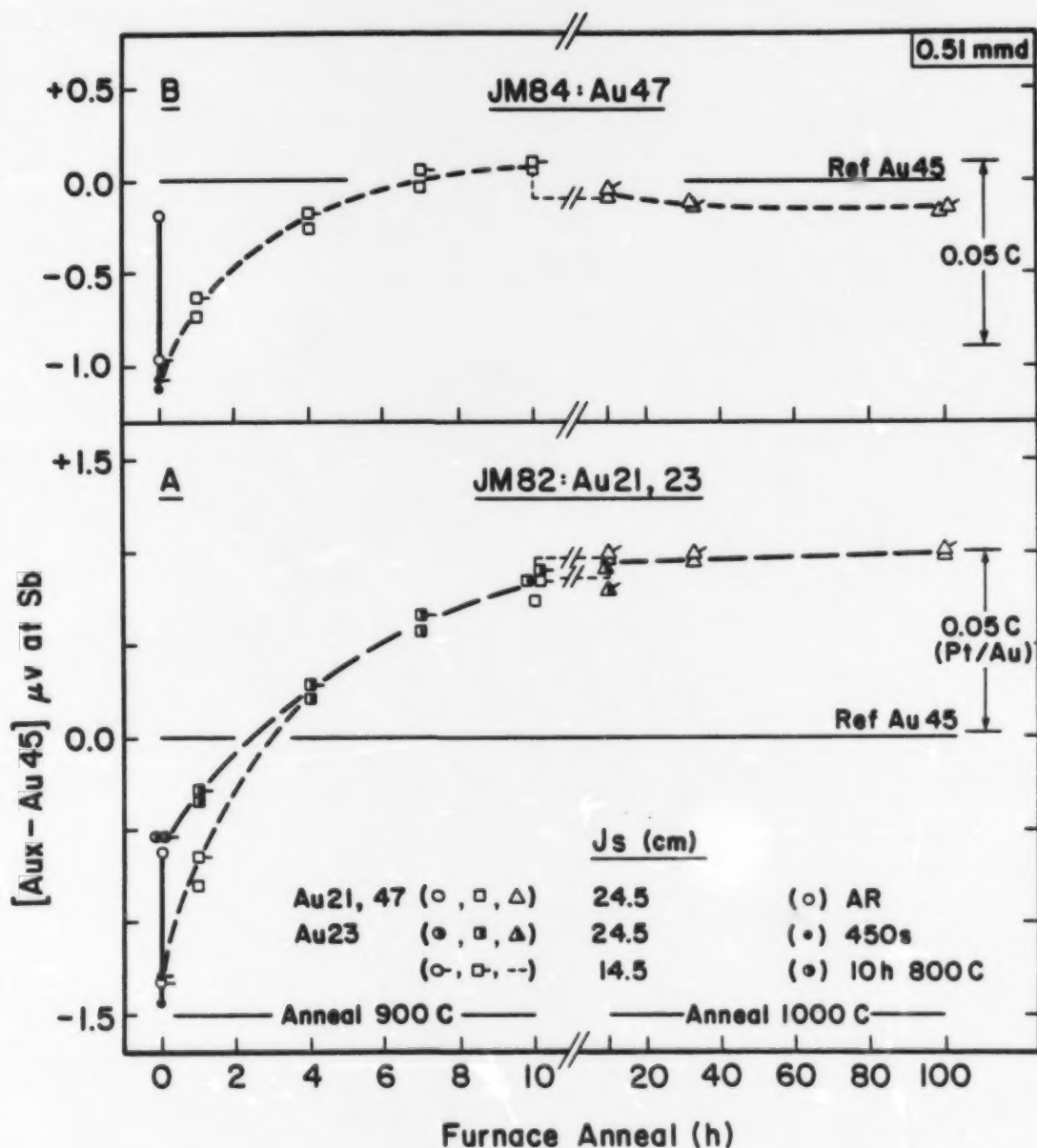


Fig. 4 Relative thermoelectric stability and homogeneity at the Sb point with duration of uniform preparatory anneals at 900°C and 1000°C on Au elements from Source JM.

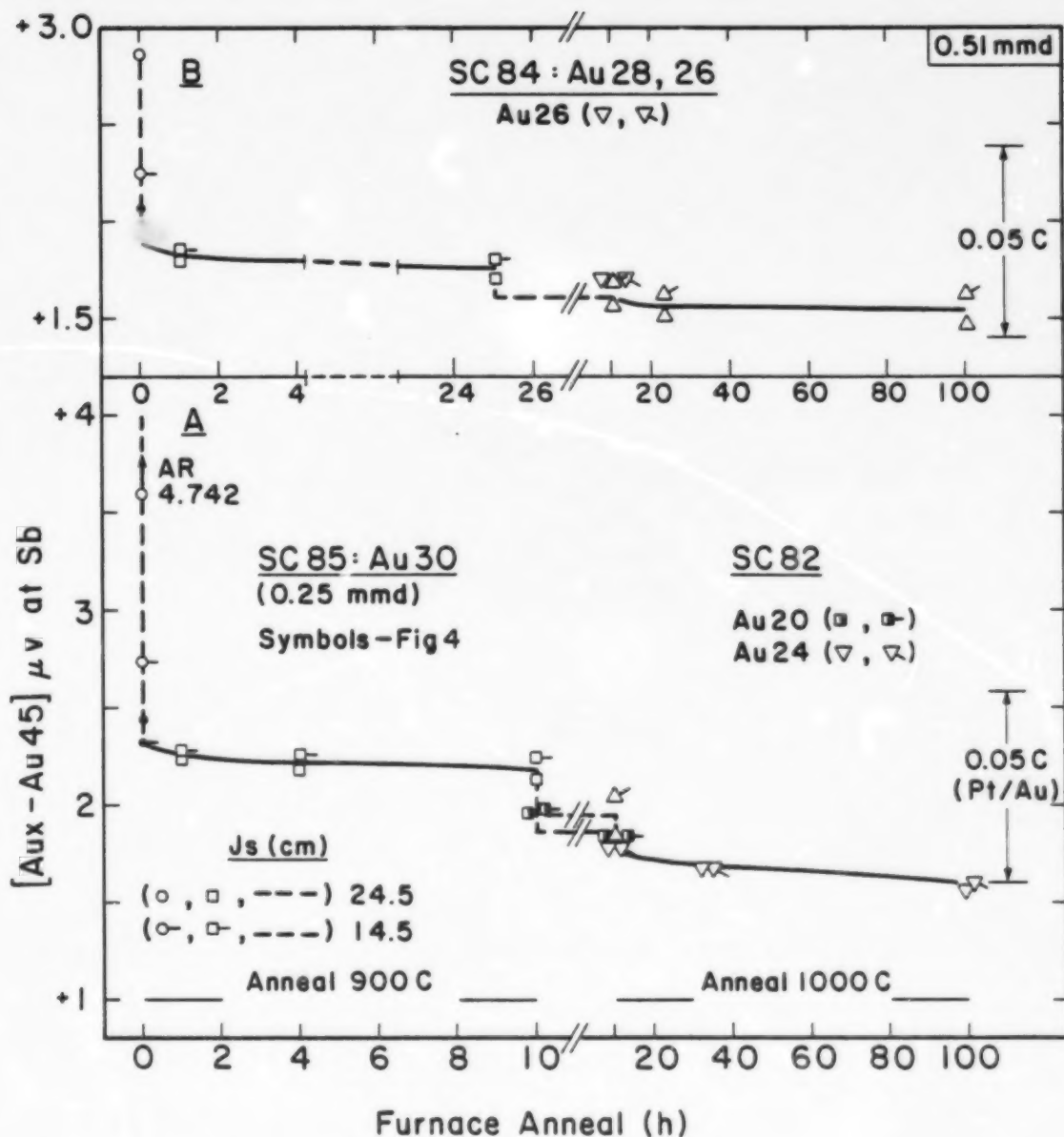


Fig. 5 Relative thermoelectric stability and homogeneity at the Sb point with duration of uniform preparatory anneals at 900°C and 1000°C on Au elements from source SC.

differences in the thermoelectric effects of FA900°C anneals on JM and SC wire most likely reflect differences in both the contents and the states (e.g. dissolved solute or oxide inclusion) of the chemical impurities in the two refined products; (3) following 10 h uniform furnace anneals at 1000°C, Figs. 4, 5 indicate that Au elements from both refiners attain and maintain high (equivalent to a variation in a Pt/Au temperature measurement of $\sim (0.01 - 0.02)^{\circ}\text{C}/100 \text{ h}$ at 1000°C) degrees of thermoelectric stability and homogeneity on further heating to 100 h; (4) the relative Seebeck TEMFs of wires initially in the AR and 450s states, undergo similar variations in sign, magnitude and homogeneity independent of refiner or batch on exposure to the Sb furnace gradient; (5) the 10 h FA800°C anneal on Au23:JM82 (Fig. 4A) merely hastens the heat-treating processes that are activated in the FA900°C anneals on JM wire; (6) as a sum-up Figs. 4, 5 clearly indicate that a $> 10 \text{ h}$ FA at 1000°C places 59 grade Au wire from these refiners in stable thermoelectric states for exposure to temperatures up to 1000°C.

d) RELATIVE THERMOELECTRIC EFFECTS OF UNIFORM HEAT TREATMENT WITH
MEASUREMENT TEMPERATURE

In the preceding sections the relative thermoelectric effects of uniform preparatory anneals on Au elements have been examined at either the Sb freezing point (Figs. 1, 2; 630.755°C) or in the Sb and Ag fixed-point furnaces stabilized at 639°C (Figs. 3A, B; 4, 5) and 967°C (Figs. 3C, D) respectively. In this section the thermoelectric effects of heat treatment on the Seebeck TEMFs of several Au elements

are determined at selected temperatures over the full range (0-1000)°C utilizing fixed-point furnaces stabilized at 160, 235, 420, 639, 786, and 967°C. The relative TEMFs measured at maximum immersions in the six fixed point furnaces stabilized at the six test temperatures are plotted in Fig. 6. [The relative Seebeck TEMFs of every Au wire listed in Table IV were measured at the six test temperatures in the range (160-1000)°C and charted, in plots similar to Fig. 6, to establish the temperature dependencies of the thermoelectric changes effected by heat-treating JM and SC elements. The Fig. 6 survey presents enough representative information to reveal the general trends that are heavily reinforced by the full body of data, too extensive to include here].

The data presented in Fig. 6 illustrates the trends of the thermoelectric changes found on annealing 59 Au wire from selected batches at selected temperatures. Some plots are truncated at the lower temperatures to avoid overlap clutter but do reveal the performance of the heat-treated wires at the higher temperatures at which the Pt/Au thermocouple should be most useful. Particular attention should be focussed on the temperature dependencies of wires heated at 1000°C, which preparation anneals have been shown (Figs. 4, 5) to yield Au wire of the highest thermoelectric stability for subsequent use as a thermoelectric sensor in the full range (0-1000)°C.

Figure 6 and similar data lead to the following generalizations: (1) the relative Seebeck TEMFs for SC wires (Figs. 6C, D) preannealed for > 1 h at 900°C and at 1000°C are directly proportional to the

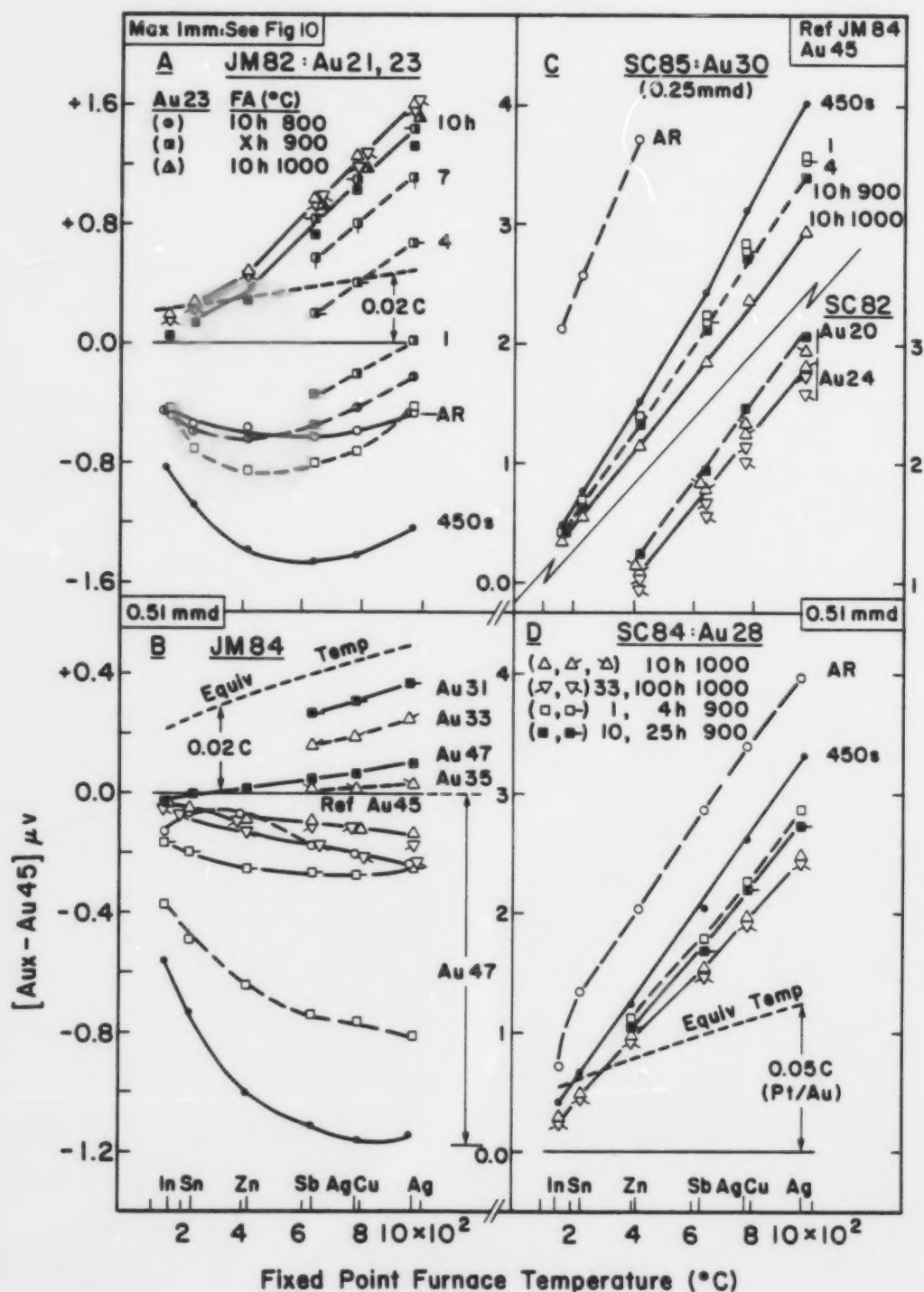


Fig. 6 Temperature dependencies of the relative thermoelectric effects of uniform preparatory heat treatments on Au elements from two sources.

measuring temperature over the full range (0-1000)°C, varying $< 0.1 \mu\text{V}$ (equiv. $< 0.01^\circ\text{C}$ in a Pt/Au temperature measurement) from a simple linear dependency; (2) the relative Seebeck TEMFs for the JM84 (Fig. 6B) wires preannealed for > 10 h at 900°C and at 1000°C are likewise linearly proportional (within $0.1 \mu\text{V}$) with measuring temperature over the full range (0-1000)°C; but, only elements Au25, 27 (Fig. 10) from JM82 duplicated this performance over the full range, the others Au19, 21, 23 (Fig. 6A) varied $< 0.1 \mu\text{V}$ from linearity over the range (400-1000)°C but diverged as much as $< 0.3 \mu\text{V}$ at 160°C; (3) the different temperature dependencies at lower temperatures and durations indicate primary thermoelectric differences in these SC and JM wires — even AR and 450s state SC wires (Figs. 6C, D) exhibit nearly linear proportionalities between relative TEMF and measuring temperature, whereas the corresponding performances on JM wires (Figs. 6A, B) indicate only gross thermal refining occurring until after 7 h FA at 900°C. Thereafter the relative TEMF varies (Fig. 6A) linearly with measuring temperature from (400-1000)°C, deviating only $0.2 \mu\text{V}$ at 160°C; (4) the greater the temperature and duration of the preparatory heat treatment on JM wire, the smaller the deviation from a linear dependency of the thermoelectric change with measuring temperature; (5) it is likely that these differences in the temperature dependencies of the thermoelectric effects of heat treatment on SC and JM wires are related to the temperature dependencies of the conduction electron concentrations and Fermi levels existing in the wires which, in turn,

are related to specific differences in impurity contents in the source wires; (6) speculatively, the distinct differences between the behavior of SC (Fig. 5) and JM (Fig. 4) wire to FA at 900°C could be associated with the removal of a single chemical impurity, perhaps Pd (see Table VI); (7) the verification of a linear proportionality between change in relative TEMF with measuring temperature following preparatory heat treatments on test elements in a Au/Au comparison couple, relative to a pre-stabilized reference element, not only enables accurate intercomparisons and interpolations between test temperatures of the relative TEMFs of Au wires from many sources at any temperature in the range (0-1000)°C but also implies that temperatures could be interpolated more accurately between calibration points on a Pt/Au thermoelectric wire scale.

e) SPECIAL CASES

1) Variations along 59 Grade Au wire drawn from the same refined batch

In the foregoing, following identical preparatory heat treatments, the magnitudes of the Seebeck TEMFs and the thermoelectric inhomogeneities along thermoelements relative to the reference element Au45 were nearly identical for all the wires examined from a particular batch of 59 grade Au wire. This indicates both that the as-delivered wire in each batch, independent of refiner, was nearly homogeneous in its physical and chemical defect contents, and that the thermoelectric

properties of each sample of the wire taken from the same batch was altered nearly identically by each specific heat treatment.

Two exceptions to this were observed — both from the same batch (SC82) . They are discussed in some detail here because such exceptions imply that occasionally substantial variations in impurity contents may exist either along wire that was contaminated during drawing or subsequent handling by refiner or user, or along wire drawn from ingots that contained pockets of segregated solutes that were not levelled by the refiners' homogenizing anneal.

The first case concerns the widely divergent differences in the thermoelectric effects of heat-treating element Au8 at temperatures and durations inferior to the preferred 10h FA at 1000°C preparatory anneal, compared to the trends established on annealing ten 62 cm lengths of wire removed from the same roll (SC82) in consecutive order and labelled in ascending even numbers from Au6 to Au24 respectively. The Seebeck TEMFs generated at maximum immersion in the Sb fixed point by these Au elements, following various preparatory anneals and referenced to platinum element Pt(P103), are listed in the chronological order of the measurements in Table IIIA. The TEMFs for element Au8 in the Pt/Au comparison couple are distinctly ($\sim 28 \mu\text{v}$ at Sb, equiv. 1.4°C) lower than the corresponding values for all (only exception Au22, discussed later) the other elements from the same batch examined in a wide variety of preparatory anneal-states.

TABLE IIIA: Thermoelectric Effects of Heat-treating SC82 Elements
Referenced to Pt(P103); Au8, Au22 Anomalous

Element Au x	Anneal State	TEMF [P103:Aux] mv at Sb ^b
6	AR	8.7198
8	1 h WA740	8.6919
10	3 "	8.7200
12	6 "	8.7200
14	10 "	8.7199
8	2 h WA740	8.6922
8R ^a	2 "	8.6925
16	1 h WA740	8.7202
16	1 WA800	8.7198
16	1 WA850	8.7198
16	1 WA900	8.7196
18	AR	8.7195
18	1 h FA800	8.7193
18	10 FA800	8.7193
20	AR	8.7201
20	1 h FA900	8.7193
20	10 FA900	8.7193
22	AR	8.7195
22	1 h FA1000	8.7154
22	10 FA1000	8.7154
24	AR	8.7199
24	1 h FA1000	8.7192
24	10 FA1000	8.7191

(a) hot junction segment reversed; (b) max. immersion

Near the completion of this study, further investigations were undertaken to help elucidate the anomalous thermoelectric behavior of element Au8 by determining the thermoelectric effects of preparatory anneals at the higher temperatures and long durations that had proven successful in the establishment of a general stabilizing anneal for most Au elements from both refiners. This time the thermoelectric effects of the preparatory heat-treatments on Au8 were made at maximum immersion in stabilized fixed point furnaces using Au/Au comparison couples referenced to element Au45. Figure 7A, graphically and Table IIIB, numerically present the variations in the relative TEMFs with measuring temperature that were determined following prior anneals at increasing temperatures and durations on element Au8; for comparison, Table IIIB also includes the corresponding data, in part charted in Fig. 6C, that was measured on a more typical wire from the SC82 batch, Au24, following uniform furnace preannealing at 1000°C.

The thermoelectric variations shown in Tables IIIA, B and Fig. 7 arising from preparatory heat-treatments on element Au8 indicate that: (1) preparatory heat-treatment on Au8 at temperatures under 1000°C failed to stabilize its thermopower to comparable values attained on annealing the other listed SC82 elements; (2) the 10 h FA at 900°C did effect a substantial increase (more positive) in thermopower (Table IIIB) but the relative TEMF at 639°C was still ~ 14 μV (equiv. to 0.7°C with Pt/Au) lower than the batch norm, as represented by Au24; (3) the 10 h FA at 1000°C effected a dramatic further positive increase in the thermopower of Au8 bringing it into

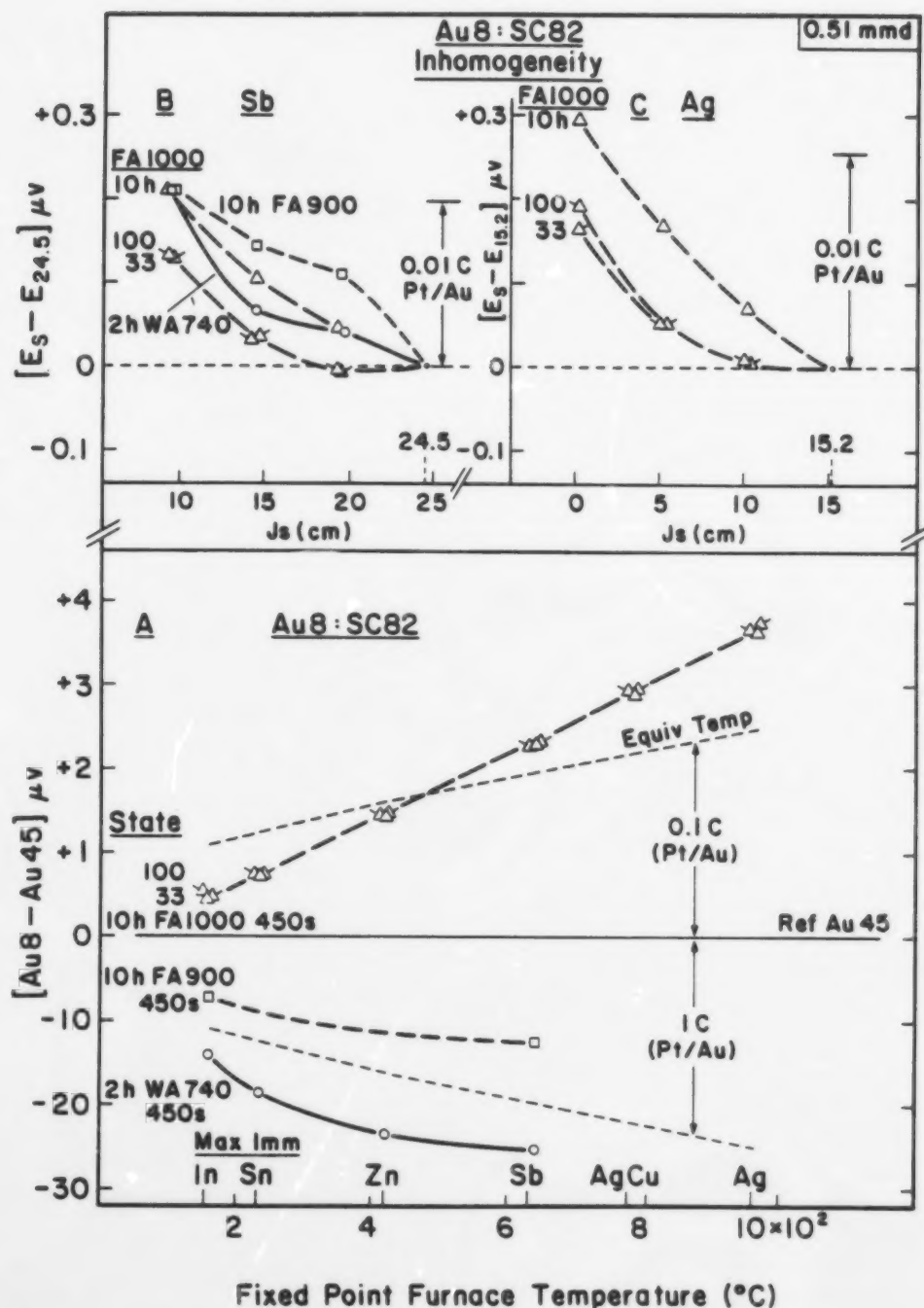


Fig. 7 A, Anomalous relative thermoelectric stability of element Au8 from batch SC82 following uniform preparatory heat treatments at temperatures $< 1000^{\circ}\text{C}$; B, C corresponding relative thermoelectric inhomogeneity along Au8 at Sb and Ag temperatures.

TABLE IIIB: Subsequent heat treatment on 59 grade SC82 elements
Au8, Au22, Au24 and 49 grade JM80 element Au49

Anneal State	160°C	Relative TEMF (Aux - Au45) μV^a					967°C
		235°C	420°C	639°C	786°C		
<u>Au8</u>							
1 h WA740	—	—	—	- 25.6	—	—	
2 WA740	- 14.0	- 18.1	- 23.4	- 25.3	—	—	
2 WA740 ^b	- 13.7	- 17.8	- 23.1	- 24.8	—	—	
10 FA900	- 7.14	—	—	- 12.34	—	—	
10 FA1000	+ 0.42	+ 0.70	+ 1.42	+ 2.29	+ 2.88	+ 3.62	
33 FA1000	+ 0.47	+ 0.74	+ 1.46	+ 2.34	+ 2.98	+ 3.74	
100 FA1000	+ 0.45	+ 0.72	+ 1.41	+ 2.26	+ 2.90	+ 3.65	
<u>Au22</u>							
10 h FA1000	- 0.38	- 0.63	- 1.44	- 1.99	- 2.52	- 3.06	
33 FA1000	- 0.47	- 0.79	- 1.72	- 2.39	- 3.01	- 3.66	
100 FA1000	- 0.48	- 0.80	- 1.74	- 2.43	- 3.03	- 3.66	
<u>Au24</u>							
10 h FA1000	+ 0.34	+ 0.56	+ 1.11	+ 1.78	+ 2.25	+ 2.82	
33 FA1000	+ 0.33	+ 0.53	+ 1.03	+ 1.68	+ 2.13	+ 2.74	
100 FA1000	+ 0.30	+ 0.48	+ 0.96	+ 1.57	+ 2.02	+ 2.58	
<u>Au49</u>							
450s	- 23.6	- 32.6	- 50.7	- 66.5	- 75.4	- 83.7	
10 h FA1000	- 2.45	- 3.67	- 6.41	- 9.90	- 12.04	- 14.29	
33 FA1000	- 2.28	- 3.44	- 6.26	- 9.31	- 11.30	- 13.40	
100 FA1000	- 2.11	- 3.20	- 5.77	- 8.52	- 10.28	- 12.15	

(a) maximum immersion

(b) hot junction segment reversed

line and even exceeding (more positive) the thermopowers of all the other lengths of SC82 wire that were examined; (4) the 33 h and 100 h FA at 1000°C further show that a high degree of thermoelectric stability to uniform exposures to the 1000°C annealing temperature had been attained in this initially unconforming length of SC82 wire in spite of its gross inferior thermoelectric performance following preannealing at lower temperatures — most probably the 1000°C heat-treatment drives a substantial chemical refinement in the element; (5) Figs. 7B, C also show that element Au8 exhibited and maintained a high degree of thermoelectric homogeneity in the Sb and Ag stabilized fixed point furnaces throughout the preparatory annealing, somewhat less but certainly comparable with the homogeneities at these temperatures measured on more typical SC82 elements Au18, 20, 24 (Figs. 8D, E) — speculatively, any degrading solutes must have been evenly distributed along the element initially and evenly removed subsequently by thermal refinement; (6) finally, Fig. 7A shows that the relative Seebeck TEMFs of Au8, referenced to Au45, following anneals at 1000°C were linearly proportional to the measuring temperature over the full range (0-1000)°C, shown earlier (section B(d)) to be a basic characteristic of the SC 59 grade Au wire examined in this study.

A second exception to the hopeful expectation of thermoelectric homogeneity and uniformity during thermal refinement along all segments of wire drawn from a single batch (SC82) of refined Au was element Au22. The relevant thermoelectric data determined for it, either in a comparison Pt/Au couple at the Sb point or in a

comparison Au/Au couple in the Sb fixed point furnace stabilized at 639°C, after preparatory FA anneals at 1000°C are presented in Tables IIIA, B and Fig. 8. These data show: (1) in AR state (Table IIIA) the Seebeck TEMFs of Au22 along the first insertion profile into the Sb point were in close agreement with corresponding values (Figs. 1C, 2B, 2D and Table IIIA) determined on companion elements Au18, 20, 24. On the W_1 profile (not shown), however, the withdrawal-TEMFs diverged as much as 3 μ V (equiv. $\sim 0.15^\circ\text{C}$) or > 3 times that observed in AR state for Au18, 20, 24 in Figs. 1D, 2B, 2D; (2) a 1 h FA at 1000°C anneal lowered (Table IIIA) the relative TEMFs at maximum immersion $\sim 4 \mu$ V from the I_1 value in AR state and this TEMF at maximum immersion remained unchanged following a total 10 h FA at 1000°C, whereas a variety of initial heat-treatments on companion elements Au18, 20, 24 from SC82 only minimally (Table IIIA) altered their thermopowers; (3) further, the IW immersion-TEMFs of the comparison Pt/Au couple in the Sb point following the 1 and 10 h heat-treatments at 1000°C were nearly identical but revealed, (Fig. 8F) a non-linear thermoelectric inhomogeneity with immersion amounting to $\lesssim 1 \mu$ V (equiv. $\lesssim 0.05^\circ\text{C}$ at Sb); (4) independent measurements of the thermoelectric inhomogeneity along the individual elements Pt(P103) and Au22 at the Sb point showed that the inhomogeneity along Au22, Fig. 8G, dominated and was the prime source of the inhomogeneity in the couple, Pt(P103) contributing $<$ the equivalent of 0.01°C to the couple's inhomogeneity at Sb; (5) following the experiments that led to the forgoing comments, Au22 was further intercompared at the six stabilized temperatures in the range

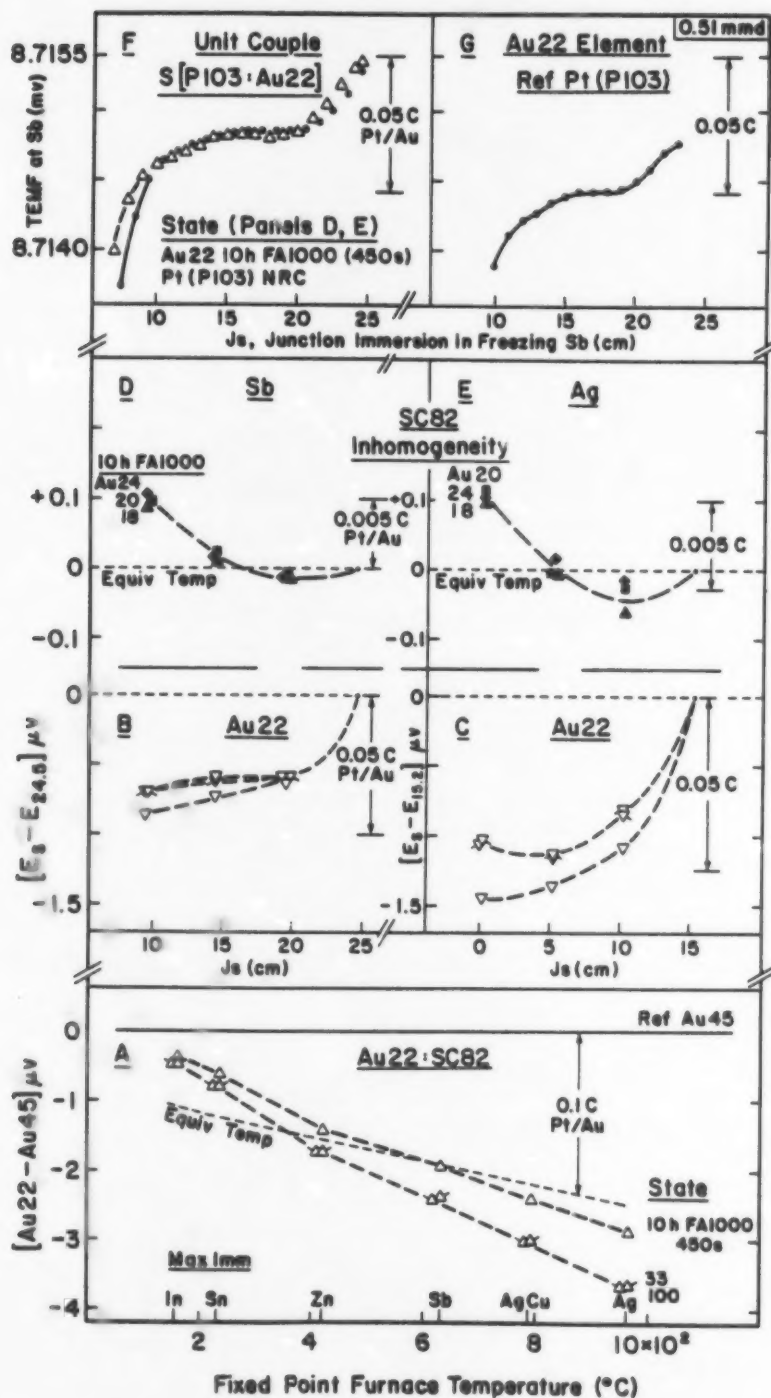


Fig. 8 Thermoelectric behavior of element Au22 from batch SC82: A, performance following uniform annealing at 1000 $^{\circ}C$; B, C and D, E, respectively, comparisons of inhomogeneities along Au22 with more representative elements from SC82 at Sb and Ag temperatures; F, G immersion characteristics in freezing Sb reveal directly inhomogeneity along Au22.

(0-1000)°C with reference element Au45 following 10, 33 and 100 h FA at 1000°C. The relative TEMFs are charted in Fig. 8A — after 33 and 100 h annealing at 1000°C the thermopower of Au22 was now stabilized but noticeably decreased (more negative) from the values attained after 10 h heat-treatment; (6) in addition, the relative TEMFs varied linearly with temperature (Fig. 8A) in the range (400-1000)°C but, similar (Fig. 6A) to elements Au21, 23:JM82, deviated from linearity by as much as $\leq 0.4 \mu\text{V}$ at the In point; (7) the TEMF inhomogeneities of Au22 at the Sb and Ag points (Figs. 8B, C) are $\sim 10\times$ greater (and equivalent to $\sim 0.05^\circ\text{C}$ in the Pt/Au measurements) than the corresponding TEMFs measured on companion elements Au18, 20, 24 and shown in Figs. 8D, E respectively; (8) following 100 h FA at 1000°C, the relative TEMF of Au22 measured at 967°C (Table IIIB) was $6.2 \mu\text{V}$ less (equiv. to -0.25°C in a Pt/Au measurement) than the relative TEMF of a more typical segment Au24 (Table IIIB, Fig. 6C) from SC82; (9) the Au22 segment is clearly a maverick in the batch and no reasonable amount of added thermal refinement succeeded in raising its thermoelectric properties close to the batch norm — probably this segment initially contained an impurity solute in the form of an oxide inclusion, which oxide dissociated under the high temperature annealing allowing the impurity to enter into a true chemical solution with the Au solvent.

Following similar heat treatments, the distinctly differing thermoelectric performances of elements Au8 and Au22 from those of the other elements from SC82, which closely conformed to a group average,

must be attributed to real chemical inhomogeneities in wire drawn from a single batch of refined Au. A consequence of finding two thermoelectrically anomalous wires in a single batch of 59 grade Au wire indicates that any Au wire selected for high (± 0.01 or 0.02°C) precision temperature measurement should have its thermoelectric homogeneity and stability on exposure to 1000°C temperatures verified by measurement.

11) Heat-treating 49 grade Au wire

As a final special case, Fig. 9 and Table IIIB show representative data, measured after heat treatments at increasing temperatures and durations on a segment of 49 grade Au wire from batch JM80 (also used earlier [2]), which lead to the following general comments: (1) not surprisingly, the thermoelectric properties of the 49 grade wire were very sensitive to preparatory heat treatment — a 100 h FA at 1000°C on element Au49 increased (more +ve, Fig. 9A, Table IIIB) the TEMF at 967°C , of the comparison couple referenced to Au45, $71.5\ \mu\text{V}$ (equiv. to 2.9°C with Pt/Au) from the corresponding relative TEMF determined after an overnight sheathed anneal at 450°C ; (2) a modicum of thermoelectric stability was attained only after substantial heat-treatment at 1000°C , a total of 100 h FA at 1000°C further increased (Table IIIB) the relative TEMF at 967°C only $2.1\ \mu\text{V}$ (equiv. $\sim 0.08^\circ\text{C}$ with Pt/Au) over the value attained after the 10 h furnace anneal; (3) the effects of heat treatments at lower temperatures (450s, FA900 $^\circ\text{C}$) fit, albeit exaggeratedly, the general trends (e.g. Figs. 4, 6A, 6B) found on the corresponding anneals on the JM 59 grade wire; (4)

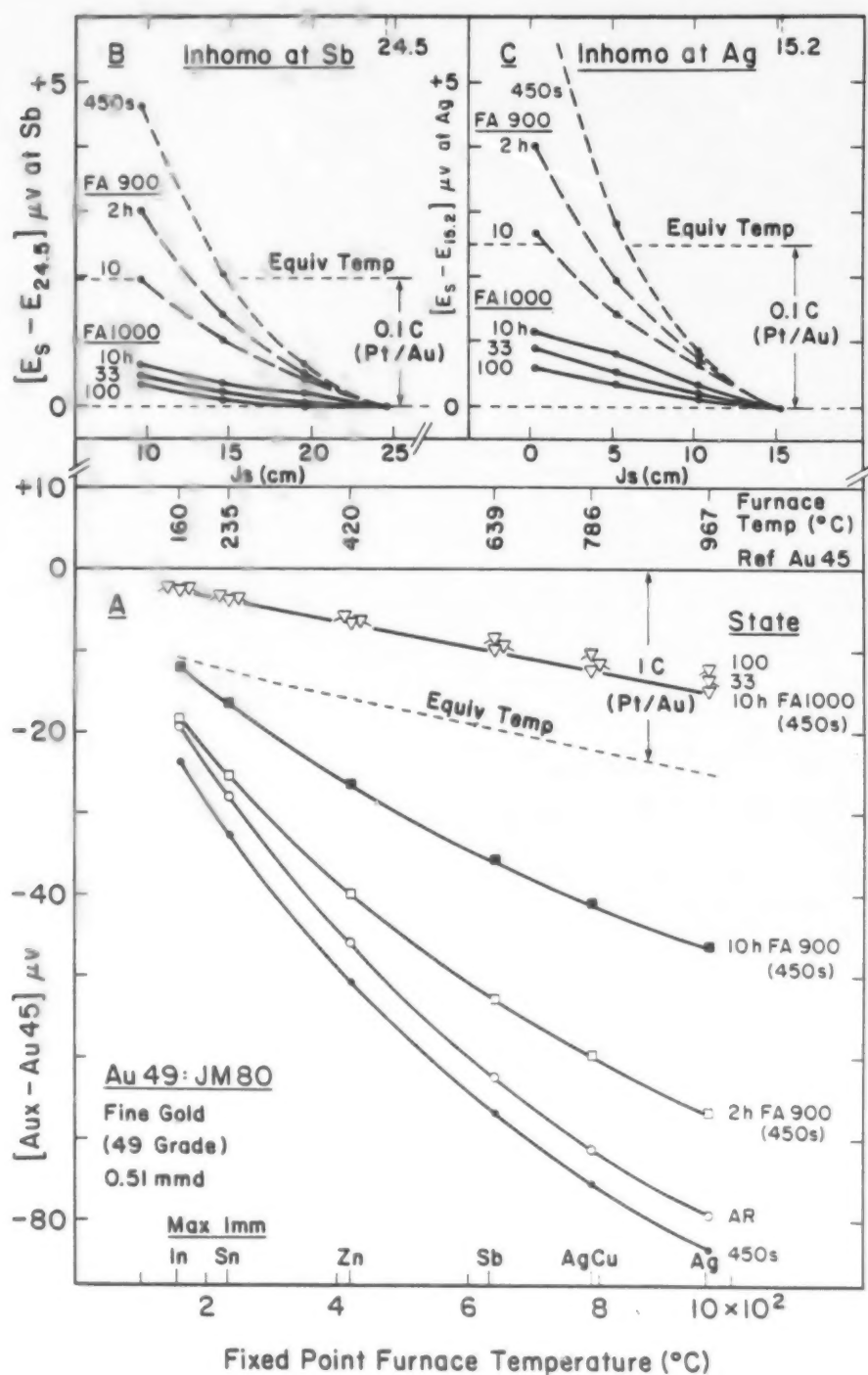


Fig. 9 A, Temperature dependency of the relative thermoelectric effect of uniform preparatory heat treatments (range 450°C to 1000°C) on element Au49 from batch JM80 (49 grade purity); B, C corresponding relative thermoelectric inhomogeneity along Au49 at Sb and Ag temperatures.

following the furnace anneals at 1000°C the relative TEMF of element 49 varied linearly (Fig. 9A, within 0.2 μ v in the range (200-1000)°C and diverging $\sim$ 1 μ v at 160°C) with measuring temperature; (5) Figs. 9B, C show how the relative thermoelectric homogeneity along a 15 cm length of element 49 at Sb and Ag furnace temperatures substantially improved on increasing the duration and temperature of the heat treatment — initial inhomogeneities equivalent to $\lesssim$ 0.16°C in temperature measurements at Sb and Ag with a Pt/Au couple being reduced nearly an order of magnitude after 100 h FA at 1000°C to, respectively, $\sim$ 0.016°C and 0.025°C, still significantly inferior to the inhomogeneities found, (Figs. 3, 8D, 8E), after corresponding heat treatments on elements of the 59 grade Au wire; (6) it is noteworthy that the inhomogeneities found (Figs. 9B, 9C) in the range (600-1000)°C along even this 49 grade Au thermoelement, prepared with a 10 h FA at 1000°C, result in temperature uncertainties in Pt/Au thermometry that are only 1/10 those found [3] on the Pt10Rh alloy thermoelements of standard couples when exposed to the same furnace temperature gradients; (7) it is clear that 59 grade Au wire (or even 69 grade, if available) should be selected as the preferred starting material from which, with further preparatory thermal refinement in the laboratory, Au thermoelements can be prepared for use in Pt/Au thermocouples intended for high precision temperature measurements.

f) PREFERRED PREPARATORY ANNEAL FOR Pt/Au THERMOELEMENTS

Based on substantial investigations of the thermoelectric effects of heat treatments on both Pt [3, 4] and Au (this paper, and

[1]) thermoelements, the NRC preferred preparatory anneals are briefly:

(1) Pt elements receive 10 h WA (refining and strain) at 1300°C followed by 1 h WA (vacancy) at 450°C; (2) 59 grade Au elements received 10 h FA (refining) at 1000°C followed by overnight FA (strain and vacancy) at 450°C; (3) the assembled Pt/Au thermocouples receive an overnight sheathed FA at 450°C.

C. THERMOELECTRIC COMPARISONS OF Au AND Pt WIRE FROM SEVERAL REFINED BATCHES

In this section, thermoelectric comparisons of Au and Pt thermoelements that have been pre-stabilized for high temperature thermometric service are presented to show the thermoelectric variations that may be found along wire inside a single batch from a single refiner, in batch-to-batch differences from a single refiner, and in batch differences from refiner to refiner. Spectrochemical analyses of some representative Au and Pt thermoelements are also presented for possible correlations with the variations found in their thermoelectric properties. It must be emphasized that these intercomparisons detect the thermoelectric properties of the thermoelements following deliberate high temperature preparatory annealing meant to stabilize thermopowers for long service at high temperature. Such anneals most likely dissociate some solutes, initially present as oxidized inclusions, and release the electrically active metallic anions into solution in the Au and Pt elements. This gives rise to degrading but measurable changes in the elemental

thermopowers. The relative thermoelectric differences among such heat-treated wires may or may not correlate with the relative differences found among the same wires in the AR state or in the states attained on annealing at the lower temperatures that are required to only remove or stabilize physical defects in strained wire.

As general working rules the purest Au thermoelement is the thermoelectrically most positive element and, in the absence of Au solute [5], the purest Pt thermoelement is the thermoelectrically most negative element. These generalizations are implied by the experimental studies of Rhys and Taimsalu [5], Cochrane [6], and Crussard [7], and are intuitively supported by plots of the standard electrode potentials [8] of the elements against atomic number which must reflect, however indirectly, relevant variations in electron energy densities, Fermi levels, electron shell structures and, therefore, thermopowers [9] of dilute alloys of electrically active solutes in the noble element Au and the transition element Pt.

a) Au WIRE

Figure 10 shows the variations in Seebeck TEMF with measuring temperature, relative to reference element Au45, that were measured on the thermoelectrically most positive Au thermoelements in each refined batch following 10 h FA at 1000°C. Table IV lists the relative TEMFs that were measured in the complete intercomparisons of every Au element in the stabilized fixed point furnaces at 639°C and 967°C following, variously, the three heat treatments, 10 h FA at 900°C and 10 h, 100 h FA at 1000°C. The final column in Table IV lists the comparison TEMFs

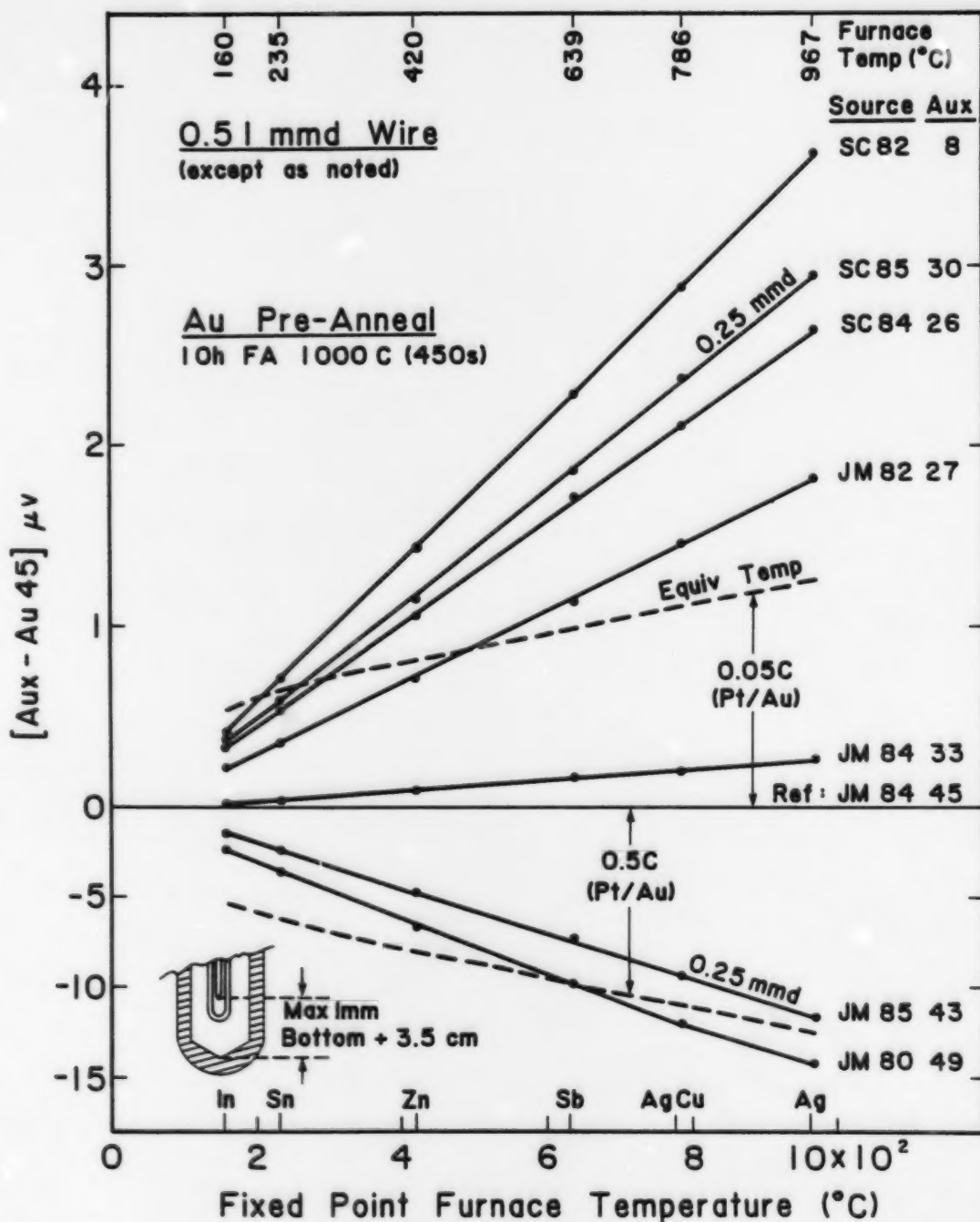


Fig. 10 Thermoelectric comparisons relative to reference element Au45 over the range 160°C to 967°C of the most positive Au thermoelement from each of seven refined batches of high purity Au wire; numerical values at 639°C and 967°C are listed in Table IV.

TABLE IV: Thermoelectric Intercomparison at 639°C and 967°C of Annealed Au Wires from Seven Refined Batches

Anneal duration at temp. (°C)			Au(x) relative to Au45 (μV) ^a										Rel. Au8 ^b																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																											
Source	Grade	Diam Wire (mm)	Uniform Furnace Pre-anneal					10 h at 1000																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																
			Comparison Temp. (°C)	10 h at 900 <u>639</u> <u>967</u>	10 h at 1000 <u>639</u> <u>967</u>	100 h at 1000 <u>639</u> <u>967</u>	10 h at 1000 <u>639</u> <u>967</u>	100 h at 1000 <u>639</u> <u>967</u>	10 h at 1000 <u>639</u> <u>967</u>	10 h at 1000 <u>639</u> <u>967</u>	10 h at 1000 <u>639</u> <u>967</u>	10 h at 1000 <u>639</u> <u>967</u>		(μV) ^a																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																										
SC82	59	0.51	Au8	18		-12.34		+ 2.29 + 3.62	+ 2.26 + 3.65																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																															

(a) Maximum immersion; (b) Rel. to Au8 in 10 h 1000 state; (c) Aux in 10 h 900 state

at 967°C determined on all the elements following the 10 h FA1000°C anneals numerically referenced to Au8, the most thermoelectrically positive Au element examined in the survey.

The thermoelectric comparisons at 967°C, excluding the anomalous element Au22 discussed earlier, indicate that: (1) the maximum variation in relative TEMF for all the 59 grade Au elements preannealed with 10 h FA at 1000°C is $< 4 \mu\text{v}$ at 967°C, equivalent to $< 0.16^\circ\text{C}$ in a temperature measurement with a thermocouple using a common Pt reference element; (2) the corresponding variation for 59 grade SC elements from three refined batches is $1.14 \mu\text{v}$ (equiv. 0.046°C) and, excluding the special case element Au8, only $0.48 \mu\text{v}$ (equiv. 0.02°C); (3) the corresponding variation for JM 59 grade elements from two refined batches is $1.96 \mu\text{v}$ (equiv. 0.08°C); (4) a variation for JM 59 grade elements in a single batch of $< 0.39 \mu\text{v}$ (equiv. $< 0.02^\circ\text{C}$); (5) the SC85 0.25 mmd Au wire was clearly thermometrically superior to the corresponding JM85 0.25 mmd wire which must be classed with the 0.51 mmd JM80 49 grade element Au49; (6) the performances for 59 grade elements following preanneals of 10 h FA900°C and 100 h FA1000°C (Table IV) give further numerical support for the selection of the 10 h FA at 1000°C as a reliable preparatory heat treatment to stabilize thermopowers in Au thermoelements intended for service to 1000°C; (7) all the SC Au elements (except Au22) are thermoelectrically more positive than all the JM Au elements and are therefore, invoking the before-mentioned general working rule,

thermoelectrically purer than the JM elements — however, a stable thermopower at 1000°C, rather than a high absolute value, is the most important requirement for a superior Au temperature sensing element and the thermoelectric stabilities of suitably-prepared JM 59 grade elements are certainly comparable with those of similarly prepared SC elements; (8) the time has not yet arrived when Au thermoelements are routinely available with a unique stabilized thermopower that would eliminate the necessity of calibrating each Au element; (9) a consistent correlation exists between the relative TEMF differences determined among the Au elements at 967°C and the corresponding values measured at 638°C due simply to the linear increase in relative TEMF with measuring temperature that was discussed earlier.

The thermoelectric comparisons of the most positive Au element in each batch with reference element Au45 at the six comparison temperatures in the full range (160-967)°C, shown in Fig. 10, further reveal high degrees of linear dependency of the relative TEMF with measuring temperature.

b) Pt WIRE

Comparable intercomparisons were made on thermometric grade Pt wire. For the Pt case, however, data will be presented on Pt elements that were prepared with 10 h 1300°C WA and 10 h 1100°C WA NRC preparatory anneals only, since more complete investigations of low and high temperature heat treatments of Pt in various metallurgical states have been described earlier [2, 3, 10] . Figure 11 shows the variations in the comparison TEMFs with measuring temperature, relative

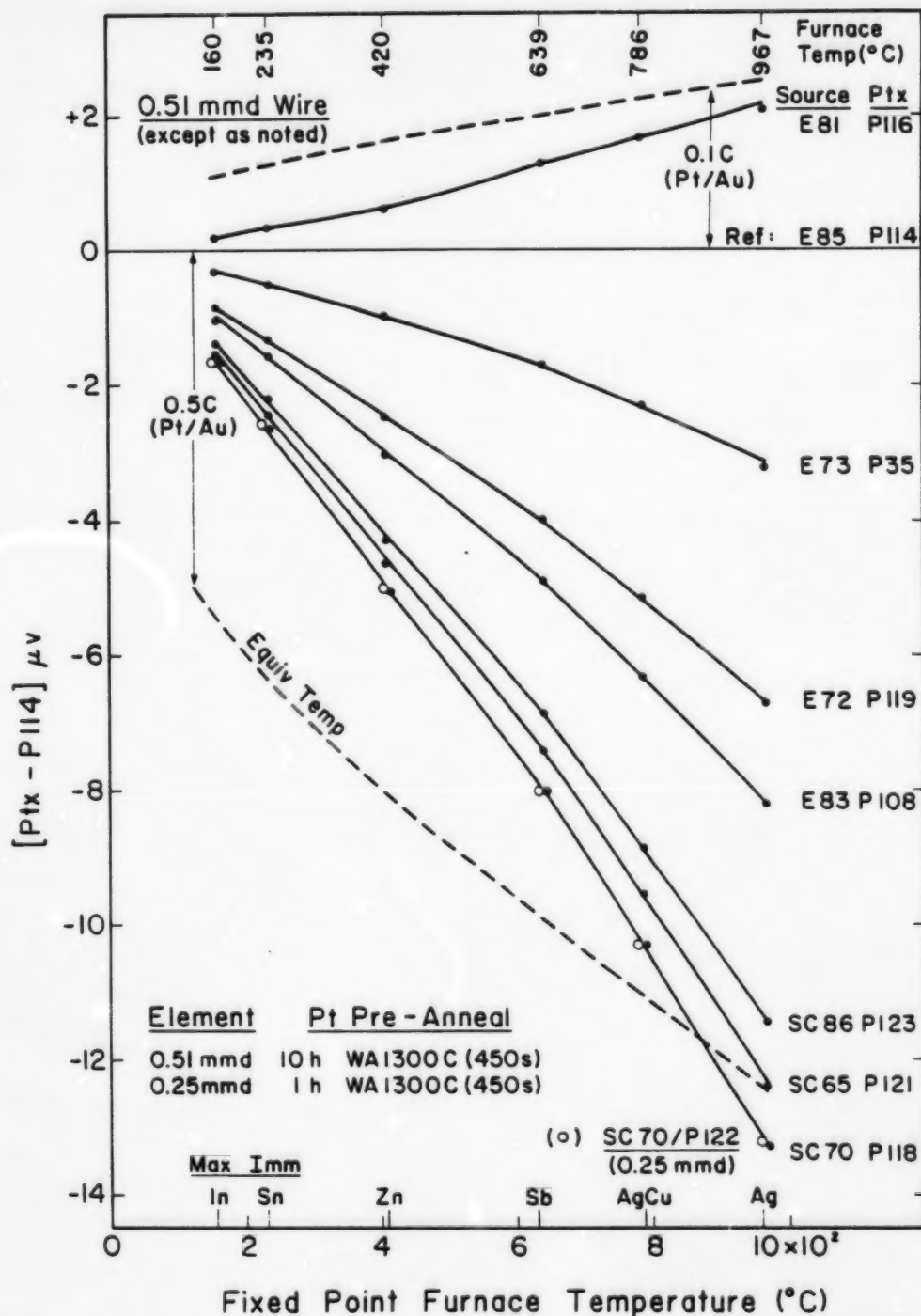


Fig. 11 Thermoelectric comparisons relative to reference element Pt(P114) over the range 160°C to 967°C of the most negative Pt thermoelement from each of nine refined batches of thermometric grade Pt wire; numerical values at 639°C and 967°C are listed in Table V.

to reference element Pt(P114), that were measured on either the only element or on the most negative (i.e. the 'purest') Pt element in each refined batch of Pt wire following NRC preparatory anneals of 10 h WA 1300°C (450s). Corresponding comparative TEMFs were also determined (not shown here) on representative Pt elements prepared in the AR, the 450s, and the 10 h 1100°C WA annealed states to look for characteristic differences in the temperature dependencies of the thermoelectric properties among elements from the two sources. Table V lists the numerical values of the relative TEMFs that were measured on all the Pt elements in the stabilized fixed point furnaces at 639°C and 967°C. Most of the elements were prepared with only initial 10 h 1300°C WA anneals; a few with initial 10 h 1100°C WA anneals, then thermoelectrically intercompared, and followed by an additional 10 h 1300°C WA and remeasured; one 0.25 mm Pt element was given a 10 h 1100°C WA and later a 1 h 1300°C WA — 0.25 mm Pt elements, following 10 h 1300°C WA anneals, are recrystallized with large grain size and are therefore mechanically weak and are easily plastically deformed or fractured during subsequent handling. The final column in Table V lists the comparison TEMFs at 967°C determined on all the Pt elements following 10 h NRC preparatory anneals numerically referenced to P118, the most thermoelectrically negative element examined in the survey.

From the intercomparisons at 967°C presented in Fig. 11 and Table V significant generalizations on the thermoelectric properties of the Pt elements prepared with the NRC 10 h 1300°C WA are: (1) for all the Pt elements the overall spread in relative TEMF was 16 μ v,

TABLE V: Thermoelectric Intercomparison at 639°C and 967°C of Annealed Pt Wires from Nine Refined Batches

Anneal Comparison Source	Temp. Diam (mm)	(°C)	Wire	Pt(x) relative to Pt(P114)(μ v) ^a			Rel. ^b Pt(P118) 10 h at 1000 967 (μ v) ^a
				10 h WAl100 (450s) 639	10 h WAl300 (450s) 639	967	
SC65	0.51		P121	- 7.36	- 7.44	-12.39	+ 0.87
SC70	0.51		SC7		- 7.88	-13.13	+ 0.13
			P118		- 8.00	-13.26	0.0
			P120	- 7.67	- 7.83	-13.01	+ 0.25
*SC70	0.25		P122	- 7.74	- 8.02	-13.22	+ 0.04
					*1 h WAl300(450s)		
SC86	0.51		P123	- 7.20	- 6.86	-11.43	+ 1.83
			P124	- 12.04	- 6.88	-11.47	+ 1.79
E72	0.51		P3		- 4.66	- 7.83	+ 5.43
			P21		- 3.92	- 6.52	+ 6.74
			P119	- 5.57	- 4.00	- 6.70	+ 6.56
E73	0.51		P35		- 1.72	- 3.20	+10.06
E81	0.51		P103		+ 1.64	+ 2.47	+15.73
			P104		+ 1.63	+ 2.53	+15.79
			P116		+ 1.26	+ 2.04	+15.30
			P117	- 1.28	+ 1.43	+ 2.13	+15.39
E83	0.51		P108		- 4.88	- 8.22	+ 5.04
			P109		- 4.67	- 7.86	+ 5.40
			P110		- 4.86	- 7.88	+ 5.38
			P111		- 4.90	- 8.03	+ 5.23
			P112		- 4.53	- 7.54	+ 5.72
E85	0.51		P114	0.0	0.0	0.0	+13.26

(a) Maximum immersion; (b) Rel. to Pt(P118) in 10 h WAl300(450s) state

equivalent to $\sim 0.64^{\circ}\text{C}$ in a thermocouple temperature measurement using a Au reference element; (2) for SC elements from four batches refined between 1965 and 1986 there is an overall variation of $1.83\ \mu\text{v}$ (equiv. 0.074°C); (3) for E elements from five batches refined 1972 to 1985 there is a variation of $10.36\ \mu\text{v}$ (equiv. 0.42°C); (4) for the limited number of samples examined, variations inside a single batch appear significantly smaller for SC wire (0.04 to $0.25\ \mu\text{v}$) than for E wire (0.49 to $1.31\ \mu\text{v}$) — these variations are first order indications of thermoelectric inhomogeneity along the wire on the individual spools; (5) SC elements were distinctly (Fig. 11 and Table V) more negative than E elements — the 'best' E element, Pt(108), being $3.2\ \mu\text{v}$ more positive (equiv. 0.13°C at 967°C with Pt/Au) than the "poorest" SC element, Pt (123); (6) slightly quadratic variations in relative TEMF with measuring temperature are suggested in Fig. 11 following the 10 h 1300°C WA (also after 10 h 1100°C WA) — in contrast to the simpler linear temperature dependency of the relative TEMF found (Fig. 10) with Au over the same range of temperature; (7) the quadratic proportionalities between relative TEMF and measuring temperature were not present in the intercomparisons of AR and 450s state wire but only develop after preparatory anneals at the higher temperatures; (8) comparison TEMFs (Table V) at 967°C on the SC Pt wire preannealed for 10 h 1100°C WA are not greatly altered (max. $+0.61\ \mu\text{v}$, equiv. $< 0.025^{\circ}\text{C}$) by an additional 10 h 1300°C WA, but corresponding heat treatments on two samples from two batches of E Pt wire indicate

substantial changes (max. $+4.9 \mu\text{v}$, equiv. 0.2°C) following the additional 10 h 1300°C WA — undoubtedly a consequence of differences in the active impurity contents in the respective thermoelements.

In sum-up, because of the large thermoelectric differences found among different refined batches of thermometric (59 grade) Pt wire, as with 59 grade Au wire, which are due to residual dissolved impurity contents, each Pt/Au thermocouple intended for precise temperature measurements in the range $(0-1000)^\circ\text{C}$ will require separate temperature calibration over the usable range — pure Pt and Au elements remain as yet an unattained objective. Separate calibrations, however, are also required for the alternative temperature sensors for the same range, either the Pt/Pt10Rh couple or the high temperature platinum resistance thermometer.

c) WIRE ANALYSES

Following the thermoelectric intercomparisons, spectrochemical analyses were made on samples of the hot junction segments of several Au and Pt thermoelements to look for possible correlations between dissolved impurity contents and thermoelectric properties. The analyzed wires were chosen on the basis of their thermoelectric performance (Tables IV and V, Figs. 10, 11) as being representative of the best, the intermediate, and the poorest elements that were examined. Table VI lists these elements, their batch numbers and impurity contents in the order of the empirical "thermoelectric purity" of the batch (Au elements in order of decreasing positiveness and Pt elements in order of decreasing negativeness). From this

TABLE VI: Relative Chemical Impurity Analyses and Comparative TEMFs of Selected Thermoelements

Source	mmd	Element	Anneal State	^a Impurity (ppm wt)						^b _{967°C} TEMF (μv)	
				Si	Mg	Fe	Pd	Ag	Cu	<u>c</u> _{rel. Au45}	<u>c</u> _{rel. Au8}
<u>Au wire</u>											
SC82	0.5	—	AR	0.06	0.1	6	—	—	—	—	—
SC82	0.5	Au20	10 h FA1000	0.06	0.03	0.3	2	0.2	0.4	+ 3.0	- 0.7
JM82	0.5	—	AR	0.1	0.05	0.3	20	—	0.1	—	—
JM82	0.5	Au27	10 h FA1000	0.06	0.02	0.3	10	0.2	0.4	+ 1.8	- 1.8
JM84	0.5	—	AR	0.02	0.02	0.3	15	0.2	0.2	—	—
JM84	0.5	Au47	100 h FA1000	0.02	0.02	0.2	1	0.1	2	- 0.2	- 3.8
JM85	0.25	—	AR	0.04	0.03	0.6	3	0.2	0.06	—	—
JM85	0.25	Au43	10 h FA1000	0.06	0.05	0.3	3	0.2	1	-11.6	-15.2
<u>Pt wire</u>											
SC70	0.5	P118	10 h NRC	0.1	0.05	0.5	2	0.1	1	0.5	0.0
E72	0.5	P119	10 h NRC	0.1	0.05	2	2	0.1	1	2	+ 6.6
E81	0.5	P116	10 h NRC	0.1	0.05	5	15	0.2	2	2	+ 2.0
											+15.3

(a) semi-quantitative spectro-chemical analyses by V. Clancy, Chemistry Div. NRC
 (b) max. imm.; (c) Table IV; (d) Table V

survey, Table VI shows that: (1) for heat-treated Pt wire, a rough correlation exists between thermoelectric negativeness and total impurity content; (2) no obvious correlations are evident between the thermoelectric positiveness and total impurity content for heat-treated Au wire from four different batches, or between heat-treated and as-received wire from the same batch.

Undoubtedly, the thermoelectric differences among suitably heat-treated wires, over the range of temperature for which a thermocouple is intended, can be more accurately and simply determined by direct measurement than by calculation using less accurate knowledge of both the impurity contents and the variations of thermopower with temperature of specific thermoelectrically active impurities in these extremely dilute alloy thermoelements. The direct measurements, furthermore, have the added capability of providing the necessary knowledge of the thermoelectric stability and homogeneity of the elements under service conditions that are required for the proper assessment of the performance of a thermocouple. Impurity analyses do provide a refiner with information that is useful in selecting or altering refining processes to improve purity but the final arbitration in wire selection must include a thermoelectric evaluation.

D. PROVISIONAL WIRE SCALE

To derive a provisional wire scale for the Pt/Au thermocouple up to 1000°C, one thermocouple [Pt(P112):Au35] was calibrated at maximum immersion in the six metal fixed points. The thermoelements were prepared with the NRC preparatory anneals; the immersion

characteristics of this couple in five of the fixed points were presented earlier in Figs. 17, 18B, 19B of reference [1].

Table VII lists the calibration data, and values of TEMF at the fixed points and at 100 K intervals over the range 0°C to 1000°C that were derived from a 5th degree polynomial fitted to the data. The values rounded to the nearest 10 mK of the calibration temperatures used in the computations for the high purity metal fixed points In, Sn, Zn and Ag are traceable to IPTS-68; the NRC Sb freezing point to reference [11]; and the freezing temperature of the AgCu eutectic is a nominal average of the determinations by Crovini and Marcarino [12] and Bedford and Ma [13]. Table VII includes the first derivatives (i.e. Seebeck coefficients) of the 5th degree polynomial at the listed temperatures and includes, for comparison, the TEMFs determined with a Pt/Au thermocouple over the same temperature range nearly 50 years ago at NBS (Washington) by Roeser and Wensel [14] — in the latter review neither the source nor preparatory heat treatments, of the Au and Pt thermoelements were given.

The 5th degree polynomial fits the calibration data within the equivalent of $< 0.01^{\circ}\text{C}$ from the Zn point to 1000°C and within $< 0.02^{\circ}\text{C}$ over the full range 0°C to 1000°C. It should provide a reasonable working temperature scale for Pt/Au thermometry until substantial intercomparisons are undertaken between the Pt/Au wire scale and the temperature scales realized variously with the standard

TABLE VII: Fixed Point Calibration of Couple [Pt(Pt12):Au35] with a Provisional Wire Scale and its First Derivatives (S) Derived from a 5th Degree Polynomial Fitted by Least-squares to the Calibration Data

Fixed Point	TEMP				Ref. [14]	
	TEMP °C	Calibration mv	Polynomial ^a mv	Residual ^b μv	INT 48 ^c mv	INT 68 ^d mv
Ice	0.0	0.0	0.0	0.000	0.0	0.0
	100		0.7776		0.78	0.78
In	156.63	1.3494	1.3496	- 0.155		
	200		1.8426		1.84	1.83
Sn	231.97	2.2340	2.2338	+ 0.210		
	300		3.1383		3.14	3.13
	400		4.6291		4.63	4.62
Zn	419.58	4.9418	4.9419	- 0.120		
	500		6.2950		6.29	6.27
	600		8.1273		8.12	8.09
Sb	630.755	8.7239	8.7238	+ 0.114		
	700		10.1234		10.13	10.10
AgCu	779.60	11.8290	11.8290	+ 0.005		
	800		12.2826		12.29	12.26
	900		14.6006		14.61	14.58
Ag	961.93	16.1111	16.1110	+ 0.099		
	1000		17.0654		17.09	17.06

(a) TEMP = $a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4 + a_5 T^5$, where $a_1 = 0.00609$, $a_2 = 1.83374 \times 10^{-5}$, $a_3 = -1.5979 \times 10^{-8}$, $a_4 = 1.2601 \times 10^{-11}$, $a_5 = -3.984 \times 10^{-15}$; (b) residual = measured- calculated; (c) Roeser and Wensel's [14] tabulated values; (d) original values converted to 1968 scale.

TABLE VIII: Extreme TEMFs Derived for Couples Formed from the 59 Grade Pt and Au Elements Intercompared in Section C.

Fixed Point °C	TEMF derived from Wire Intercomparisons			
	H, Highest	L, Lowest	Spread	
	[Pt(P118):Au8] mv	[Pt(P104):Au47] mv	H-L μv	H-L equiv °C
0	0.0	0.0	0.0	0.0
156.63	1.3504	1.3480	2.4	0.22
231.97	2.2358	2.2319	3.9	0.31
419.58	4.9454	4.9379	7.5	0.46
630.755	8.7296	8.7176	12.0	0.61
779.60	11.8364	11.8210	15.4	0.70
961.93	16.1204	16.1009	19.5	0.79

Pt/Pt10Rh thermocouple, the high temperature platinum resistance thermometer, and the photoelectric pyrometer.

As a final aspect, Table VIII lists the highest and lowest TEMFs at the fixed points with thermocouples resulting from pairing Pt and Au thermoelements, prepared with the preferred NRC preparatory anneals, from the selection of 59 grade elements intercompared in this work.

CONCLUSIONS

This study shows that 59 grade pure Au wire from two refiners may be heat-treated into states of high thermoelectric homogeneity and stability which, when combined with adequately preannealed high purity Pt thermoelements into a Pt/Au thermocouple, are capable of functioning to temperature measurement precisions of the order of $\pm 0.01^\circ\text{C}$ in the range $0-1000^\circ\text{C}$.

Thermoelectric comparisons, following preferred preparatory heat-treatments on Au and Pt elements selected from many refined batches of wire produced by several refiners, show: (1) a ready availability of wire of suitable purity for such measurements; and (2) for the wider view, the thermoelectric differences to be expected in wire selected from a single refined batch and from batch-to-batch and refiner-to-refiner.

A 5th degree polynomial fitted to a fixed point calibration of a Pt/Au thermocouple provides a simple provisional working wire

scale for temperature interpolations between fixed points pending more substantive temperature scaling researches.

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